THE RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS OF NITRIC OXIDE

THESIS SUBMITTED BY

WILLIAM A. SEDDON, A.R.I.C.

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

UNIVERSITY OF EDINBURGH

DECEMBER, 1962.

ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to Dr. H.C. Sutton for his enthusiastic encouragement, unstinted advice and unflagging support throughout the whole of this work.

In addition I am indebted to Professor N. Feather, F.R.S., for the opportunity to work on this project, the laboratory facilities and financial support during the last three months.

Thanks are also extended to the technical staff, in particular Mr. A. Headridge, Mr. R. Haldane and Mr. W. Wilson, for their prompt attention to a variety of requests, both directly and indirectly connected with this work.

Finally, I would like to thank Dr. T.W. Woodward for reading the manuscript and suggesting various alterations, and also to D.S.I.R. for a maintenance grant.

INDEX

INDEX (contd.)

INDEX (Contd.

CHAPTER I

INTRODUCTION

Chapter I

Introduction

(1) General

Radiation chemistry can be defined as the study of all chemical changes resulting from the interaction of high energy radiations with matter. Within this sphere a vast amount of work has been done and no attempt will be made here to give a comprehensive account of the general development and scope of the many fields of research. The experiments of several groups in the early part of this century, chiefly concerned with gas phase reactions, are however summarised in a monograph by Lind[1]. Of all these fields, the study of the effects of radiation on water and aqueous solutions has probably been the most thoroughly investigated, a situation partly the result of their obvious relevance to radiobiology. The work to be presented and discussed in this thesis is confined to such studies.

(2) The Radiation Chemistry of Water and Aqueous Solutions

Contemporary thinking on the radiation chemistry of water stems from the careful studies of Fricke[2], on the X ray induced oxidation of ferrous sulphate in 0.8N sulphuric acid solution. The ultimate application of this system as a chemical dosimeter laid the foundations for the accurate study of radiation induced reactions in solution, and a special issue of Radiation Research[3], pays tribute to this pioneering work. Recent literature is very extensive but a book by Allen[4], and a review by Hart and Platzman[5], serve as excellent introductions to the subject. The main aspects in this field

involve the study of the elementary processes occurring on the absorption of radiations in water; the identification and assay of radiation products, the elucidation of reaction mechanisms and the detailed study of competitive kinetics.

The various processes by which high energy radiations interact with matter are amply discussed elsewhere.[6-8] In aqueous solutions irradiated with Co^{60} γ rays the absorption takes place predominantly via Compton scattering, the photo-electric effect being only important below about 200 KeV and in solutions containing solutes of high atomic number. Pair formation is of little significance. The excited molecules, ions and electrons initially produced rapidly give rise to the formation of reducing and oxidising species, generally accepted as H and OH radicals.[9] Also observed are the molecular products hydrogen and hydrogen peroxide in yields so nearly constant for a given quality of radiation, that these are also regarded as primary products. The reducing specie is now known to exist in at least two forms each with different kinetic behaviour, whilst recent studies have demonstrated that the oxidising specie, which could conceivably occur in more than one form, is best represented by the conventional formula, OH.[10,11] A more detailed discussion of the former aspect is presented in a later section.

These primary radical species are located in the immediate vicinity of the track of the incident radiation and consequently formed in regions of high concentration, the distribution of which is dependent upon the quality and energy of the incident radiation. With γ rays an irregular array

of radicals, in an approximately spherical region (or spur), are distributed along the path of the radiation whilst the spurs produced by alpha particles lie very close together and coalesce into a continuous track. A competition therefore exists between a recombination of these radicals and their diffusion away from each other. The formation of H_2 and H_2O_2 has generally been attributed to such diffusion controlled reactions but a contribution from non radical interactions may well be significant. Platzman,[12] invokes processes involving the dissociative attachment of subexcitation electrons to water molecules to account for a fraction of the hydrogen yield as in

$$H_2O + e^-_{s.e.} = OH + H^-$$
$$H^- + H_2O = OH^- + H_2$$

and also[13] that interactions between excited H atoms or OH radicals (H^* and OH^*) and water, may well contribute to the yields of molecular H_2 and H_2O_2, respectively

$$H^* + H_2O = H_2 + OH$$
$$OH^* + H_2O = H_2O_2 + H$$

The fraction of radicals which do escape recombination are subsequently detected by their reaction with solutes present in the bulk of the solution.

A quantitative interpretation of the action of radiation on an aqueous solution is based on a knowledge of the amounts of molecular H_2 and H_2O_2 and the free radicals formed, together with a description of the subsequent reactions undergone by these entities in a given solution. The basic quantities of radical and molecular yields are

expressed in terms of the number directly produced per 100 eV of energy absorbed in the solution, and are denoted by the symbol G, followed by a subscript as G_{H_2}, $G_{H_2O_2}$, G_H and G_{OH}. The methods used to obtain these particular values, which for Co^{60} γ radiation are connected by the equation of material balance

$$G_{-H_2O} = G_H + 2G_{H_2} = G_{OH} + 2G_{H_2O_2}$$

are amply illustrated elsewhere.[4,14] These values can vary with solute concentration, a reduction in the molecular yield with a corresponding increase in the radical yield being due to the increasing interference of the solute with the normal radical recombination process in the spurs. Much more marked effects are observed with a variation in quality of the incident radiation; the molecular product yields of H_2 and H_2O_2 increasing with increasing LET (Linear Energy Transfer), while the corresponding yield of free radicals decreases. This latter observation is consistent with the greater concentration of radicals produced along the track of a densely ionising particle.

Theories to account for the concomitant diffusion and kinetics of radicals from a particle track were stimulated by the aforementioned effect of radiation quality on the yields of the primary products. A successful theoretical interpretation depends on a knowledge of many parameters of which the initial distribution of the primary reactive species is of major importance. In the simple model first suggested by Lea,[15] (and later Platzman[16] for slightly different reasons), it was assumed that the H and OH radicals were distributed

initially according to symmetrical Gaussian functions with the H atoms spread much further away from the axis of the particle track than the OH radicals. Assuming a reasonable value for the diffusion coefficient and that every collision between H and OH was effective, this model successfully predicted the gross features of the above effect. Samuel and Magee[17] departed from this view and suggested that both species were formed by the dissociation of excited water molecules and therefore had the same initial Gaussian distribution. Using values for the various parameters of reasonable orders of magnitude, this theory gave good agreement with experiment for the fraction of radicals combining to give molecular products in a γ ray track. Kupperman[18] shows that the initial distribution of H atoms cannot be very much wider than that of the OH radicals if the sole mechanism of formation of primary H_2 and H_2O_2 is a recombination between H or OH radicals in the spur. Platzman,[12] as indicated previously, does however suggest alternative modes of formation of H_2 and H_2O_2. Irrespective of these basic anomalies the radical diffusion model is capable in its more refined forms of explaining the finer aspects of radiation chemistry,[18] and justifies its further application in the interpretation of experimental data.

(3) <u>The relation of aqueous radiation chemistry to radiobiology together with the oxygen and nitric oxide effects.</u>

A distinctive feature of radiobiology is the extreme sensitivity of a living cell to small quantities of absorbed radiation; a dose may be sufficient to kill an organism and yet be undetectable with an ordinary chemical system. Since

living cells contain about 85% water a great deal of work was originally undertaken on the radiation chemistry of solutions with the aim of understanding such marked effects. This ideal is as yet far from realisation.

Much of the early work is discussed in the classic book by Lea,[15] At this time it was established that in aqueous suspensions of biological material, two modes of action could be distinguished, (i) indirect and (ii) direct. The former was attributed to the interaction of the water free radicals with the substrate and the latter to the direct absorption of energy within the substrate itself. It was further recognised that the indirect action could be readily modified and inhibited by the addition of organic substances as radical scavengers, the sensitivity then being associated with direct action alone. Furthermore the extreme sensitivity of a cell was explicable in terms of the "target" hypothesis. The basis of this theory was that within a biological structure there existed certain vital target molecules, the integrity of which was essential if the system was to function in its normal manner. This function could be destroyed if a single ionisation occurred within this target. Extensive work has since been conducted on the modification of the effects of radiation by a variety of chemical and physical agents and this, as Alper[19] points out, has without real justification, tended to overestimate the importance of the indirect effect at the expense of the target theory.

Among the substances known to modify radiation injury to cells, the enhancing role of oxygen has been the subject of

numerous investigations. Reviews by Gray[20,21] admirably survey this aspect. In general it is found with X or γ radiation that the dose required to inactivate a given cell or tissue suspension is two to three times as great when anaerobic as when aerobic. Furthermore oxygen is active at very low concentrations and in the great majority of cases it is found that the sensitivity is positively correlated with its concentration, in the immediate environment of the cell, at the time of irradiation.

A consideration of the similar properties of nitric oxide with oxygen led Flanders[22] to investigate the effect of the former gas on the radiosensitivity of bacteria (Shigella flexneri). It was found in experiments conducted under strict anoxia that the sensitivity was raised to a level normally associated with the aerobic condition, and this finding was subsequently extended to effects on higher cells by Kilhman[23] using anoxic Vicia faba roots, and Gray[24] with Ehrlich ascites tumour cells. Flanders and Jockey[25] were subsequently able to show that the effects of nitric oxide and oxygen could be correlated molecule for molecule.

Although these studies have shown that the action of nitric oxide may simulate that of oxygen, certain differences do exist in the effects of these two gases when dry biological materials are used. Powers et al.[26] found that dried spores of Bacillus megaterium were protected by nitric oxide when this gas was admitted either during or after an irradiation in nitrogen. Similarly Sparrman[27] et al. found that while nitric oxide augments the radiation induced damage to wet

plant seeds, it would protect dry seeds against such damage.

Although these irregularities do exist, the marked similarity between the effects of nitric oxide and oxygen cannot be ignored and it was this aspect which stimulated the present investigation on the radiation chemistry of nitric oxide in aqueous solution.

(4) Objects of the present work

Whilst a great deal of work on the radiolysis of solutions containing dissolved oxygen has contributed much to our present knowledge in radiation chemistry, prior to the work to be presented in this thesis no such information was available for solutions containing nitric oxide.

The role of oxygen is adequately explained in terms of its reaction with H atoms

$$H + O_2 = HO_2$$

and the subsequent reactions undergone by this entity either with itself or OH radicals

$$HO_2 + HO_2 = H_2O_2 + O_2$$
$$OH + HO_2 = H_2O + O_2$$

or in alternative oxidative reactions with other solutes present in the same solution, such as the well established oxidation of ferrous ion,

$$Fe^{2+} + HO_2 + H^+ = Fe^{3+} + H_2O_2.$$

Like oxygen, nitric oxide is one of the few stable molecules possessing an unpaired electron and is well known for its efficiency as a radical scavenger. In a qualitative fashion one might therefore expect nitric oxide to behave similarly to oxygen, but necessarily giving rise to different products.

Possible reactions are therefore

$$H + NO = HNO$$

perhaps followed by

$$HNO + HNO = N_2O + H_2O.$$

Furthermore, contrary to that found with oxygen, nitric oxide may be expected to react with the OH radical as in

$$OH + NO = HNO_2.$$

The principal objects of the present work were therefore threefold -

(i) To determine the products, their yields, and hence suggest a reaction mechanism for the γ radiolysis of nitric oxide in aqueous solution;

(ii) To confirm this mechanism by competitive kinetic studies, and at the same time obtain data which could be correlated with that well established for oxygen, in particular a determination of the relative rates of reaction of "H atoms" with nitric oxide and oxygen;

(iii) Consider such data with regard to its possible relevance and application in radiobiology.

CHAPTER II

GENERAL EXPERIMENTAL TECHNIQUE

Chapter II

General Experimental Technique

(1) Preparation of Purified Water

Water was first distilled in a commercial "Manesty" still, the distillate being collected via all glass tubing in a suitable pyrex flask. The distilled water was then refluxed overnight in alkaline potassium permanganate, finally being redistilled from this solution at the rate of about 2 litres per day. It was usual to discard the initial 150 - 200 mls. of such redistillations. Freshly purified water obtained direct from the receiver was used throughout in all experiments. A perspex box, fitted with a sliding base, enclosed the outlet from the receiver and prevented contamination with dust from the atmosphere.

(2) Cleaning of glassware

All glassware used in the radiation chemical experiments was thoroughly cleaned prior to use by standing overnight in fresh "chromic acid" cleaning mixture. The vessels were then thoroughly rinsed, first with distilled water, then purified water and finally with the solution under investigation.

(3) Radiation Vessels

All glass graduated 20 ml. "Summit" syringes were used throughout. These greatly facilitated the ease with which solutions of nitric oxide could be investigated with the complete exclusion of air. The syringes were however modified by carefully sealing a B5 cone, with as short a

stem as possible, on to the end of each syringe so as to act as a universal nozzle fitting (Plate 1). 5 ml. volumes of solution delivered by single and independent syringes, based on calibrations with distilled water, were reproducible to within $\pm$ 0.5 - 1%.

(4) Preparation of Nitric Oxide in aqueous solution

Nitric Oxide reacts readily with oxygen to give nitrogen dioxide, a mixed anhydride, which on solution in water yields a mixture of nitrous and nitric acids.

$$2NO + O_2 = 2NO_2 \quad .....(1)$$

$$2NO_2 + H_2O = HNO_2 + HNO_3 .(2)$$

Consequently the preparative procedure was largely concerned with the exclusion of air and the removal of traces of nitrogen dioxide. A ready measure of the efficiency of this process was given by the observed nitrite concentration in the prepared nitric oxide solutions. The flow system finally adopted is discussed in full below. Preliminary preparations were however unsuccessful, solutions of nitric oxide containing approximately 10^{-4}M nitrite ion. Only a part of this measured concentration was in fact produced in the preparative stage, later work showing a fraction was due to the inclusion of air in the steps involved for the analysis of nitrite. This latter aspect was however completely resolved and the method is described in Chapter III (2). Other modifications in technique to eliminate the remaining nitrite impurity included the following -

(i) All rubber tubing and rubber to glass junctions were discarded since measurements carried out in this

Plate 1.

laboratory showed that oxygen could readily diffuse through such connections.

(ii) Cold finger traps at -78°C, to freeze out any nitrogen dioxide (f.pt -9°C) were lightly packed with glass wool to increase their efficiency. Similar traps at -120°C (obtained with a slurry of 40-60 grade petroleum ether and liquid nitrogen) proved unsatisfactory, completely adsorbing all the nitric oxide.

(iii) Failure to effectively remove the residual nitric oxide from the system prior to further preparations was also a significant source of nitrite.

The following procedure using the all glass apparatus depicted in Figures 1(a) and 1(b) proved to be satisfactory in all respects. Nitric oxide was generated by a modification of the method due to Blanchard.[28]

Reagents: (i) 278g. A.R. $FeSO_4 \cdot 7H_2O$ and 55 ml. of concentrated sulphuric acid per litre.

(ii) 15g. A.R. $NaNO_2$ per 250 ml. water.

Procedure.

The apparatus as shown in Figure 1(a) was thoroughly deaerated by the passage of a stream of oxygen free nitrogen (supplied by the British Oxygen Co. Ltd.), all joints being lightly greased and held firmly in position. 250 ml. of ferrous sulphate solution, diluted 1:1, were then placed in the litre vessel B, and deaerated by allowing the nitrogen to flow out through tap b. The collecting apparatus shown in Figure 1(b) was then attached at the point S, grease being excluded from all joints in direct contact with the

Figures 1(a) and 1(b)

Apparatus for the preparation of nitric oxide in aqueous solution

Figure 1(a)

1 and 5	Traps lightly packed with glass wool and immersed in a slurry of solid CO_2 and acetone. Temperature -78°C.
2	Concentrated sulphuric acid.
3	50% potassium hydroxide solution.
4	Solid sodium hydroxide pellets.
6	Magnetic stirrer.

Figure 1(b)

1	Sintered disc, porosity 1.
D	Dilute acid ferrous sulphate solution.
S	Point of attachment to apparatus in Figure 1(a).

Figure (1a).

Apparatus for the Preparation of Nitric Oxide in Aqueous Solution.

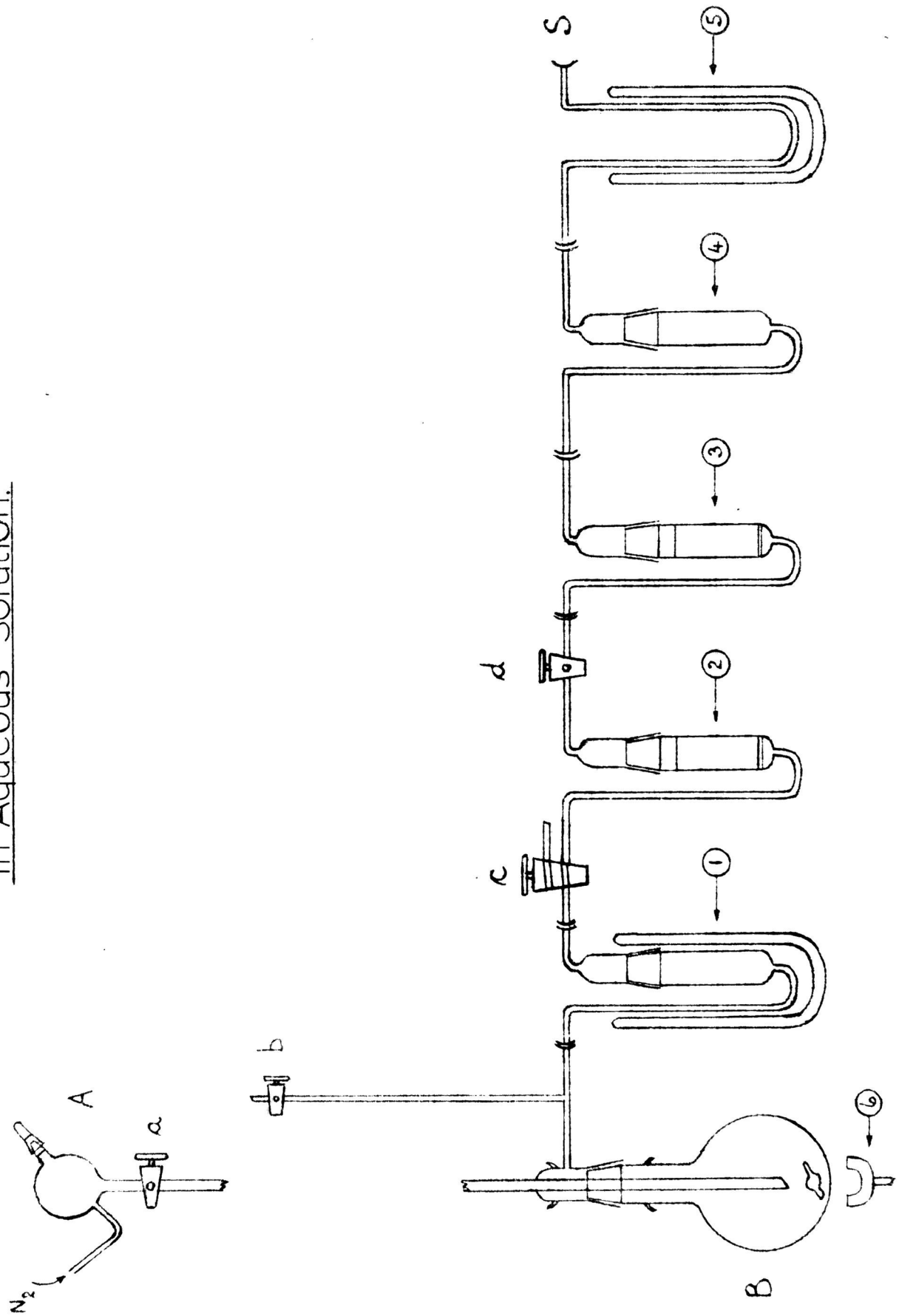
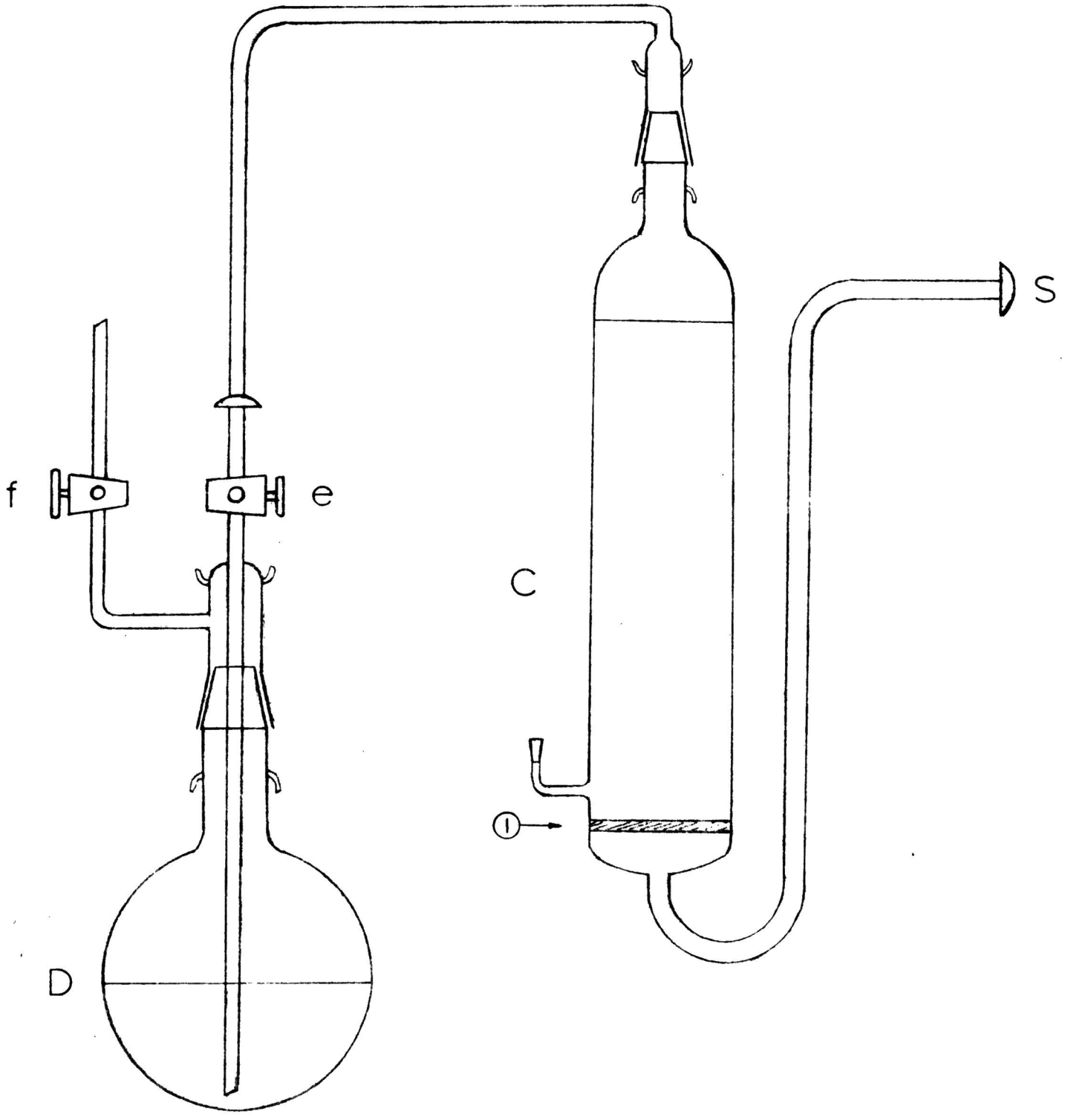


Figure (1b).

Apparatus for the Preparation of Nitric Oxide in Aqueous Solution (continued)



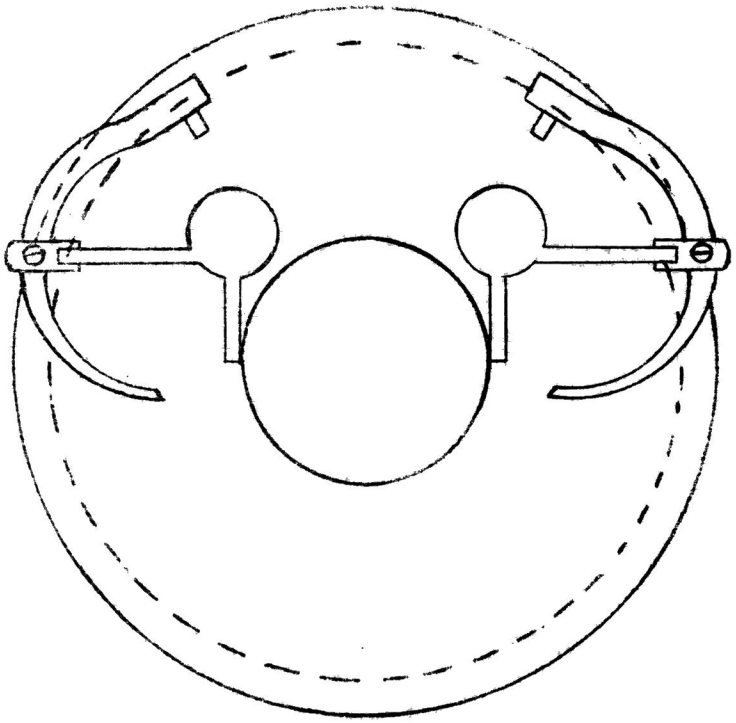
purified water or solution contained in vessel C. Vessel C of approximately 100 ml. capacity possessed four side arms (only one is shown in Figure 1(b)) terminating in B5 sockets to which the air free syringes were connected. The solution in C was then finally deaerated by passing nitrogen through the whole of the apparatus. Thorough mixing of the solution in the side arms and syringes was ensured by alternately closing and opening tap e. It was normal to allow 15-30 minutes for complete deaeration and a concentration of oxygen less than 10^{-6}M was inferred from measurements made with a Hersch[29] cell. Taps f, e and c were then closed and 250 ml. of deaerated sodium nitrite solution in A was allowed to run slowly into the ferrous sulphate solution with continuous stirring, the initial gas flow escaping through tap b. Samples were taken after equilibration of the solution with nitric oxide, by closing tap e and allowing the syringes to fill beyond the 20 ml. graduation. Spring clips were then quickly attached to prevent drainage on reopening tap e. The syringes were then capped using sealed off B5 sockets filled with solution ejected from the syringes. The four syringes so prepared were found to contain identical concentrations of nitric oxide to within $\pm$ 1%, the only detectable impurities being nitrite, always less than 5×10^{-6}M and a trace of nitrous oxide approximately 5 to 10×10^{-6}M. It was usual to use only three of these syringes for the subsequent experiments, the fourth being maintained as a blank. Prior to further preparations the residual nitric oxide was removed from the system by a stream of nitrogen

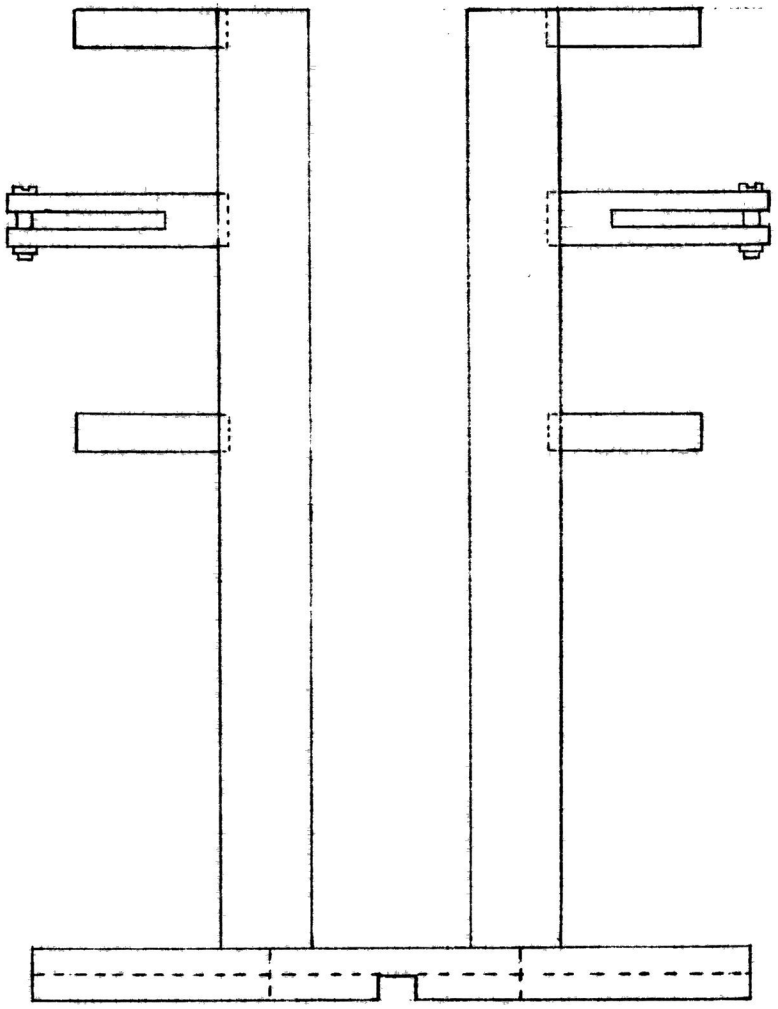
and the cold traps dried at 120°C in an air oven.

(5) Irradiation procedure and dosimetry

Two sources of radioactive Co^{60} were used throughout as the source of γ rays. The major portion of the work was carried out with a source of approximately 30 Curies, latterly increased in strength to 120 Curies. Syringes containing 15 ml. of solution were supported with the aid of the brass jig shown in Figure 2, and then exposed to the γ radiation from the Co^{60} source which could be placed quickly and reproducibly at the centre of this jig. Doses so delivered were inferred from separate calibration experiments in which the syringes were filled with the Fricke chemical dosimeter solution. Intimate mixing of the solution after irradiation was ensured by inverting the syringes several times prior to ejecting aliquots for analysis. The concentrations of ferric sulphate produced in such solutions were determined by the absorption of ferric ion at 305 $m\mu$ (using a Unicam spectrophotometer, model SP500) taking the molecular extinction coefficient as 2130 at 20°C, with a positive temperature coefficient of 0.7% per degree. The amount of energy received by each syringe was calculated using $G_{(Fe^{3+})}$ = 15.5 molecules per 100 eV. This corresponded to maximum dose rates of approximately 1.0 and 4.4 x 10^{21} eV/litre/hour or 18 and 70 kilo. rads/hour, respectively, for the weaker and stronger sources. The geometry was such that doses so inferred were reproducible to within $\pm$ 0.5% for any given side of the jig. Doses simultaneously received by syringes in each half of the jig

Irradiation Jig.





Scale: Approx. $\frac{3}{4}$ Full Size.

Figure 2

differed by about 17% for the weaker source and 25% for the stronger source.

CHAPTER III

ANALYTICAL METHODS

Chapter III

Analytical Methods

All spectrophotometric analyses were carried out using the Unicam SP500 spectrophotometer. 1 cm. quartz spectrophotometric cells were used throughout and the optical densities of reagent blanks and solutions compared against distilled water.

(1) Analysis of Nitric Oxide

(a) Preliminary work involved the oxidation of nitric oxide solutions to nitrate and then colorimetric analyses for the latter. Complete oxidation to nitrate could be readily achieved by shaking a mixture containing 5 ml. of nitric oxide solution, 0.5 ml. of 5% potassium persulphate, and 0.2 ml. N. potassium hydroxide.

$$2NO + 3K_2S_2O_8 + 8KOH = 2KNO_3 + 6K_2SO_4 + 4H_2O.$$

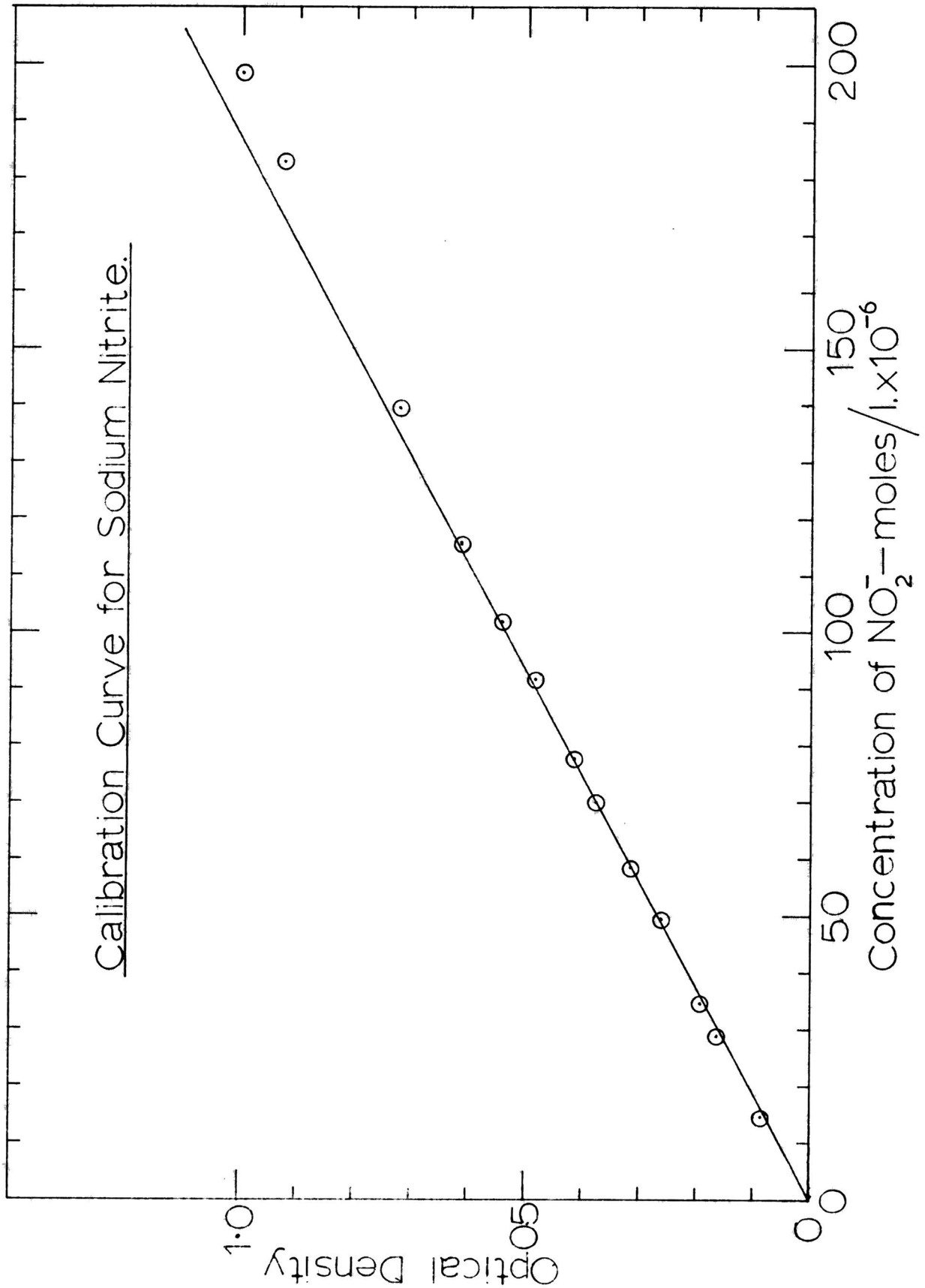
A similar procedure, but using slightly alkaline solutions of hydrogen peroxide in place of the persulphate did not achieve complete oxidation. The method was however discarded due to the somewhat tedious procedure and inaccuracy of the nitrate analyses. (See section 3).

(b) The method of analysis used throughout was based on the conversion of nitric oxide to nitrite which could then be quickly and accurately determined. The nitrite was analysed in a similar manner to that of Wilkinson,[30] which was based on the original method of Shinn.[31] Nitric Oxide was converted to nitrite by ejecting 5 ml. of solution into approximately 90 ml. of water previously saturated with oxygen, shaking vigorously and then diluting

to 100 ml. in a volumetric flask. An aliquot of this solution, in general 5 ml., was placed in a 50 ml. graduated flask, 1 ml. of 5N hydrochloric acid and 5 ml. of 0.2% aqueous sulphanilamide were then added. After allowing the solution to stand for 3 minutes, 1 ml. of 0.1% aqueous N - (1 - napthyl) ethylenediamine dihydrochloride was added and the solution allowed to stand a further 3 minutes, after which time the colour of the red azo dye was fully developed. The solution was then diluted to a final volume of 50 ml. prior to analysis. A check on the absorption maximum of the azo dye confirmed the value of 540 millimicrons ($m\mu$) and all subsequent measurements were then made at this wavelength. The molar extinction coefficient was determined in separate calibration experiments using 5 ml. aliquots of stock solutions prepared from A.R. sodium nitrite, previously standardised against potassium permanganate. A plot of the optical density as a function of the nitrite concentration is shown in Figure 3. A slight deviation from Beer's law was observed and throughout the experiments nitrite solutions yielding optical densities in excess of 0.60 were diluted and reanalysed. The value of 53,200 for the molar extinction coefficient, E, was deduced from the slope of the curve and was in excellent agreement with that obtained by Allen[32] (53,000), and 4% greater than that of Wilkinson[30] (51,200). Successive determinations on standard solutions were reproducible to within $\pm$ 0.5%.

A preliminary investigation of this method indicated that every g. mole. of nitrite so produced resulted from the

Figure 3


Calibration Curve for Sodium Nitrite.
Optical Density
0·0
0·5
1·0
0
50
100
150
200
Concentration of NO_2^- — moles/l. $\times 10^{-6}$

oxidation of an equivalent amount of nitric oxide. On the basis of the known gas phase reaction of nitric oxide and oxygen and the subsequent reaction of nitrogen dioxide with water (equations 1 and 2),

$$2NO + O_2 = 2NO_2 \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$2NO_2 + H_2O = HNO_2 + HNO_3 \quad \ldots\ldots\ldots \quad (2)$$

a ratio of 1 g. mole. of nitrite to 2g. moles. of nitric oxide was anticipated. To investigate therefore the stoichiometry of this oxidation in aqueous solution the following experiments were carried out.

(i) A number of solutions of nitric oxide were analysed by methods 1(a) and 1(b) respectively. The result obtained by method 1(a) was then compared quantitatively with that obtained by 1(b).

(ii) Aqueous solutions of nitric oxide were prepared by bubbling nitric oxide through distilled water for periods of up to 30 minutes. These solutions were assumed to be saturated and the results of their analysis by method 1(b) were compared with the known solubility of nitric oxide in water.

(iii) Samples of nitric oxide were extracted from solution using the vacuum line (Figure 7) as described in Section 5(e). The concentration of nitric oxide deduced from the volume of gas extracted per ml. was then compared with that derived by method 1(b).

(iv) 5 ml. volumes of nitric oxide solutions were converted to nitrite by reacting with 45 mls. of solutions containing different concentrations of dissolved oxygen. Concentrations of the latter were approximately 1.4×10^{-3}M,

0.8×10^{-3}M, and 0.3×10^{-3}M. Each solution was then analysed for nitrite by method 1(b).

(v) The nitrite solutions prepared in (iv) were then analysed for nitrate as described in section 3.

The results of these experiments are presented in Tables 1 and 2, and are consistent, within experimental error, with a 1:1 stoichiometry for the oxidation of nitric oxide to nitrite by method 1(b).

This is explicable on the basis of the following reactions

$$2HO + \tfrac{1}{2}O_2 = N_2O_3 \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

$$N_2O_3 + H_2O = 2HNO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

probably best written as

$$NO + \tfrac{1}{2}O_2 = NO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$$NO_2 + NO + H_2O = 2HNO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

reaction (6) being known to be very rapid.[33]

(2) Analysis of Nitrite together with Nitric Oxide

Suspected products of irradiation included nitrite and nitrate together with the residual nitric oxide. The analysis for nitrite and nitric oxide involved two steps.

(i) Determination of nitrite plus nitric oxide by reacting with oxygen as in 1(b) above, and

(ii) the determination of residual nitrite alone, after removal of the nitric oxide. The apparatus depicted in Figure 4, was employed for removing nitric oxide in step (ii) as follows:- 5 ml. of solution were ejected via the B5 socket into 5 ml. of deaerated buffer solution at a pH of about 5.2. The continuously flowing stream of nitrogen was

TABLE I

Experiment	Concentration of Nitric Oxide (x 10^{-3}M)			
	(a) Via Nitrate	(b) Via Nitrite	(c) Via Solubility	(d) Via extraction of gas/ml.
(i)	1.04 1.87 1.25) 1.41)	0.92 1.84 1.29		
(ii)		1.92 2.03 1.95	At 20°C 2.05	
(iii)		1.77 1.84		1.83 1.94

TABLE 2

Experiment		Concentration of Oxygen (x 10^{-3}M)		
		1.4	0.8	0.3
(iv)	Concentration of Nitric Oxide via Nitrite (x 10^{-3}M)	1.49 1.37 1.67	1.51 1.39 1.70	1.42 1.40 1.69
(v)	No nitrate was detected in any of the solutions associated with experiment (iv).			

Figure 4

Apparatus for the removal of nitric oxide

1 Inlet for oxygen free nitrogen.

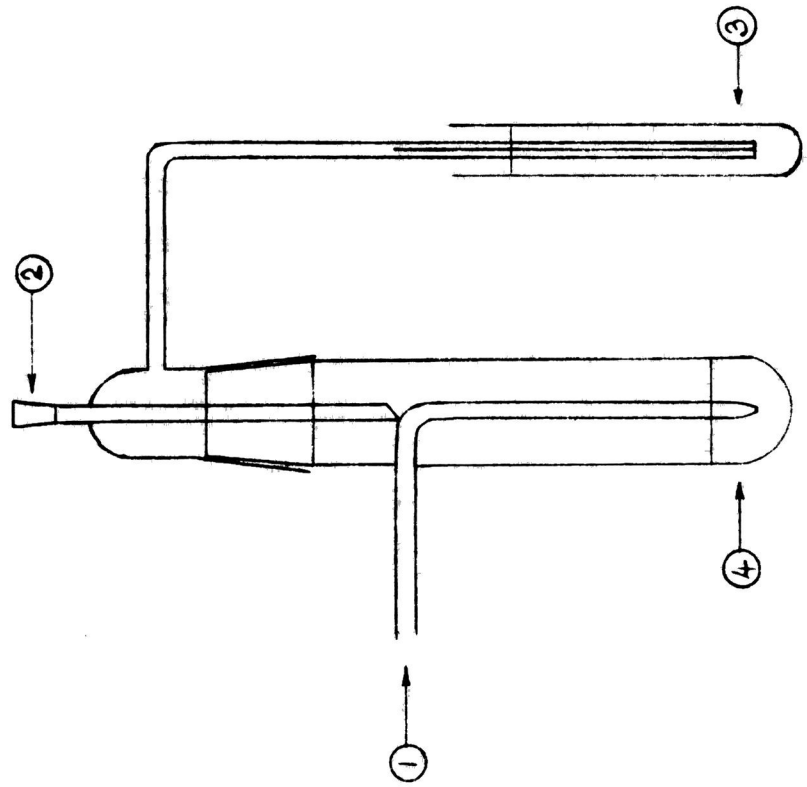
2 B5 socket.

3 Distilled water air trap.

4 Buffer solution pH 5.2

Figure 4

Apparatus for the removal of Nitric Oxide.



effective in removing first the oxygen from the buffer solution, and secondly the nitric oxide from the combined solutions in a total of less than 6 minutes. A buffer solution was necessary to prevent the decomposition of nitrite ion which would occur at a more acid pH.

$$3HNO_2 = H^+ + NO_3^- + 2NO + H_2O$$

The buffer was prepared by diluting 50 ml. of 0.2M potassium hydrogen phthalate and 30 ml. of 0.2M sodium hydroxide to a final volume of 200 ml. with distilled water.[34] These particular reagents were chosen to avoid possible interference in the analyses for hydrogen peroxide, subsequently carried out on aliquots of this same solution (see section 4). Evaporation losses were shown to be negligible and neither hydrogen peroxide or nitrate interfered with the analysis. Blank determinations with nitric oxide alone showed that no air gained access to the solution since the concentration of nitrite detected in such experiments was always less than 5×10^{-6}M.

Errors in these analyses for nitrite were largely governed by the inaccuracies in estimating the volume of solution delivered by the syringe. These "syringe errors" were more significant in the analyses to determine the consumption of nitric oxide during an irradiation, this quantity being derived from three independent measurements via 1(b), 2(i) and 2(ii). Gross errors for nitrite production and nitric oxide consumption by these methods were about $\pm$ 2% and $\pm$ 5%, respectively.

(3) Analysis of Nitrate

Analyses for this suspected product were performed

by the method of Snell,[25] utilising phenol-di-sulphonic acid.

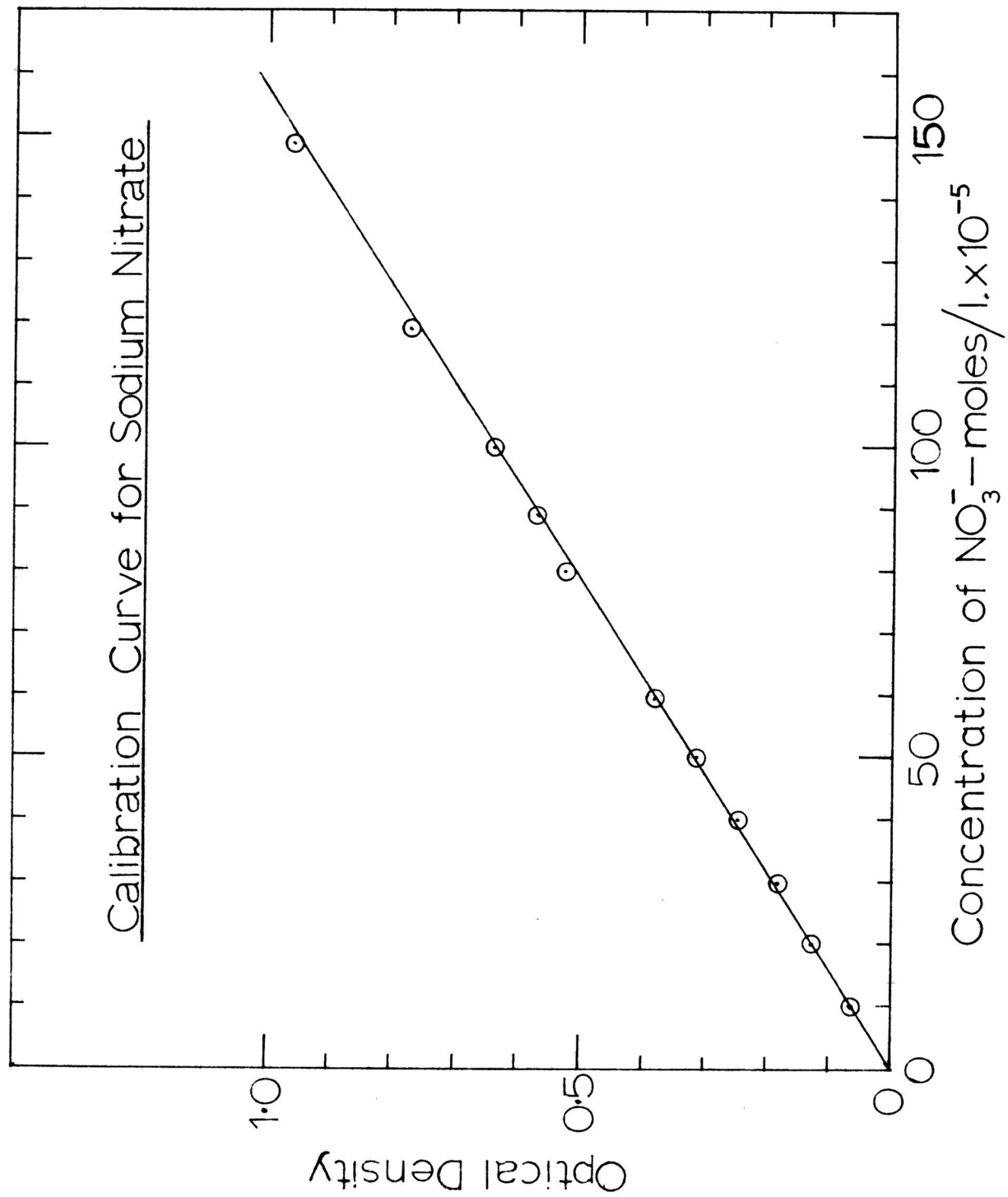
Preparation of reagent

25g. of A.R. phenol was dissolved in 150 ml. of concentrated sulphuric acid and 50 ml. of fuming sulphuric acid (containing approximately 20% of free SO_3). The mixture was heated on a boiling water bath for two hours and then allowed to cool.

Method of Analysis

Calibration experiments using stock solutions prepared from A.R. sodium nitrate were performed in the following manner. 5 ml. of the nitrate solution was transferred to a porcelain dish and rendered alkaline with 0.1 ml. of N. sodium hydroxide. The solution was then evaporated to dryness on a steam bath. On cooling 2 ml. of phenol-di-sulphonic acid were added and the mixture allowed to stand for 5 minutes. This solution was transferred to a graduated flask and rendered alkaline with 10 ml. of concentrated ammonia solution (0.88 NH_3) before diluting to a final volume of 50 ml. The yellow nitrated phenolic acid so obtained was found to absorb at 405 $m\mu$ and all subsequent analyses were carried out at this wavelength. Figure 5 shows a plot of the optical density against the nitrate concentration, the points representing the average of at least three determinations since duplicate analyses were subject to about $\pm$ 3% variation. The value of the molar extinction coefficient obtained from the slope of the curve was E = 6,350. This can be compared with the value of 6,520, deduced from Allen's[32] paper.

Figure 5


Calibration Curve for Sodium Nitrate
Optical Density
0
0.5
1.0
0
50
100
150
Concentration of NO_3^- — moles/1. x 10^{-5}

On irradiated solutions the nitric oxide was first removed as in (ii) above and an aliquot of this solution then taken for analysis. Nitrite which interferes with the analysis was removed prior to the addition of sodium hydroxide, by reacting with sulphamic acid

$$NH_2SO_3H + HNO_2 = N_2 + H_2SO_4 + H_2O$$

This reaction is rapid and 0.1 ml. of the acid readily destroys 5 ml. of 10^{-3}M nitrite ion. The total error expected in these analyses for nitrate was approximately $\pm$ 5%.

(4) Analysis for Hydrogen Peroxide

Hydrogen peroxide was determined by the method of Ghormley.[36]

Reagents. "A" 33g. potassium iodide
1g. sodium hydroxide
0.1g. ammonium molybdate

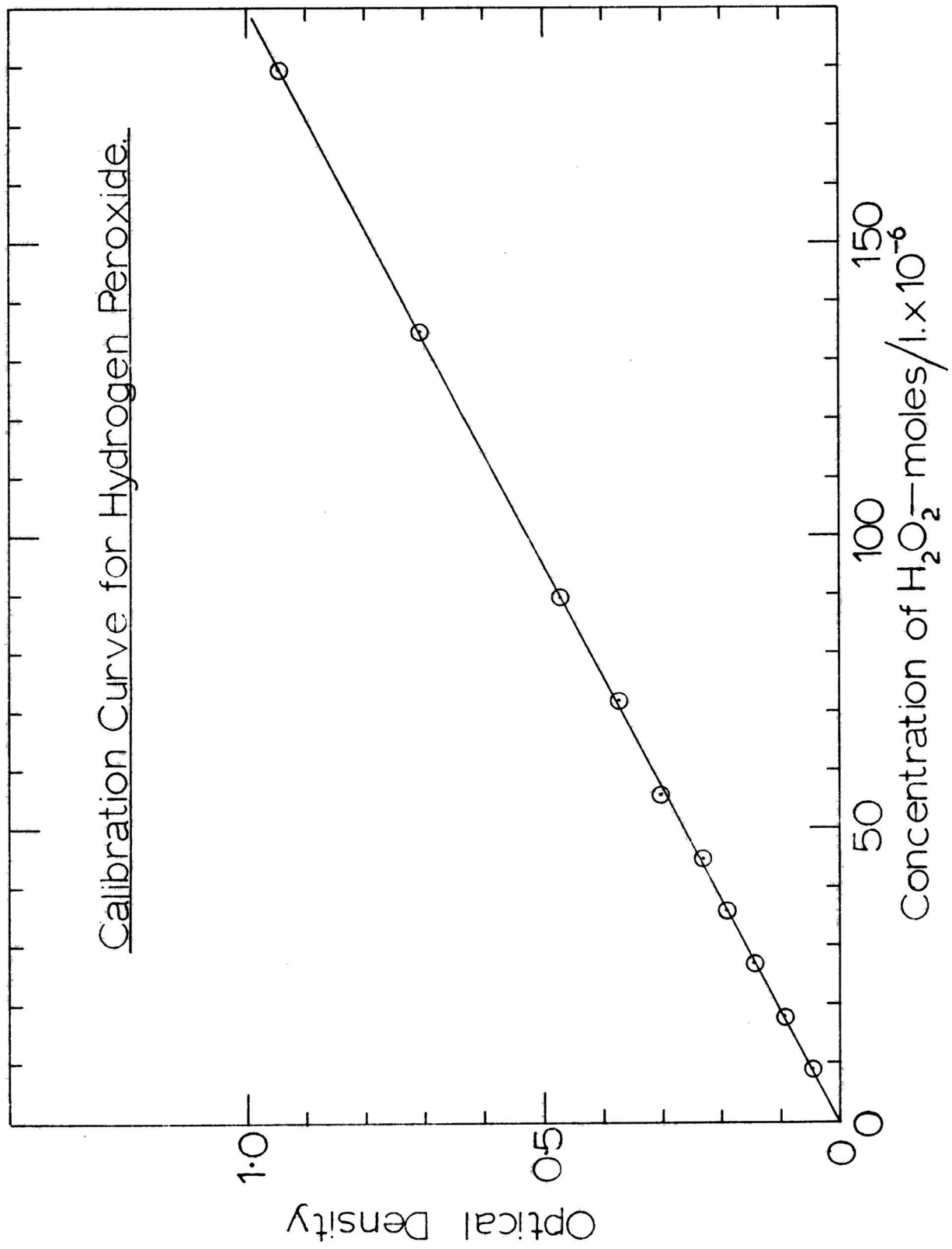
all dissolved in 500 ml. of distilled water.

"B" 10g. potassium hydrogen phthalate

dissolved in 500 ml. of distilled water.

The iodide reagent was prepared immediately prior to use by mixing equal volumes of the solutions A and B. Calibration experiments were carried out using stock solutions freshly prepared from 30% A.R. hydrogen peroxide, previously standardised against potassium permanganate. 5 ml. of the iodide reagent were added to 2 ml. of the peroxide solution and the mixture diluted to a final volume of 10 ml. in a volumetric flask. The optical density of the tri-iodide complex was measured at a wavelength of 350 mμ and expressed as a function of the peroxide concentration (Figure 6). From the slope of the curve a value for the molar extinction

Figure 6


Calibration Curve for Hydrogen Peroxide.
Optical Density
0·0
0·5
1·0
0
50
100
150
Concentration of H_2O_2—moles/1.x10^{-6}

coefficient of 26,350 was determined. This was in excellent agreement with the value of 26,400 for the I_3^- ion given by Awtrey and Connick.[37]

The effect of nitrite, which slowly oxidises iodide ion and could therefore interfere with the above analysis, was investigated in the following experiments.

(a) Solutions of hydrogen peroxide containing added nitrite ion were analysed as above and the optical density observed as a function of time following the addition of the reagents.

(b) The above solutions were reanalysed but with the addition of 0.1 ml. of 5% sulphamic acid prior to that of the iodide reagents.

(c) The results obtained with hydrogen peroxide solutions analysed in the normal manner were compared with those obtained in the presence of 0.1 ml. of 5% sulphamic acid over the full range of optical density. The results are shown in Tables 3 and 4.

It was found that a peroxide analysis could readily be completed within 3 minutes and in such time no increase in optical density, in the presence of 10^{-4}M nitrite ion, was detected.

Furthermore sulphamic acid did not interfere with the analysis.

On irradiated samples the nitric oxide was first removed as in (ii) above, and 2 ml. aliquots of this solution then taken for analysis. If such solutions contained less than 10^{-4}M nitrite ion it was usual to analyse by both methods 4(a) and 4(b). With greater concentrations of nitrite, 4(b) was adopted.

TABLE 3

Experiment	Concentration of added NO_2^- (x 10^{-4}M)	Time (minutes)	Optical Density	Concentration of H_2O_2 (x 10^{-6}M)
4(a)	0.54 1.11 0.94	2 to 6 2 to 6 2 to 6	0.091 0.211 0.182	17.3 40 34.5
4(b)	0.54 1.11 0.94	2 to 6 2 to 6 2 to 6	0.091 0.206 0.181	17.3 39.1 34.3

TABLE 4

Experiment 4(c)

The effect of sulphamic acid on the optical density of hydrogen peroxide solutions

Optical density of H_2O_2 solution	0.069	0.089	0.183	0.193	0.371	0.464	0.925
Optical density of H_2O_2 solution in the presence of sulphamic acid	0.071	0.088	0.185	0.195	0.367	0.460	0.925

(5) Gas Analysis

The gaseous products of irradiation to be suspected and fully investigated were nitrous oxide and hydrogen. A technique involving the extraction and collection of the dissolved gases from solution and their subsequent analysis was developed. The analytical procedure, based on a Gas Chromatographic method due to Graven,[38] also enabled the efficient separation of oxygen, nitrogen and nitric oxide. A quantitative study for the analysis of the latter three gases was not undertaken. The apparatus and its construction are discussed in the sections 5(a)(b)(c)(d) and the technique in sections 5(e)(f) and (g).

(a) Vacuum Line for the extraction and collection of the dissolved gases from solution.

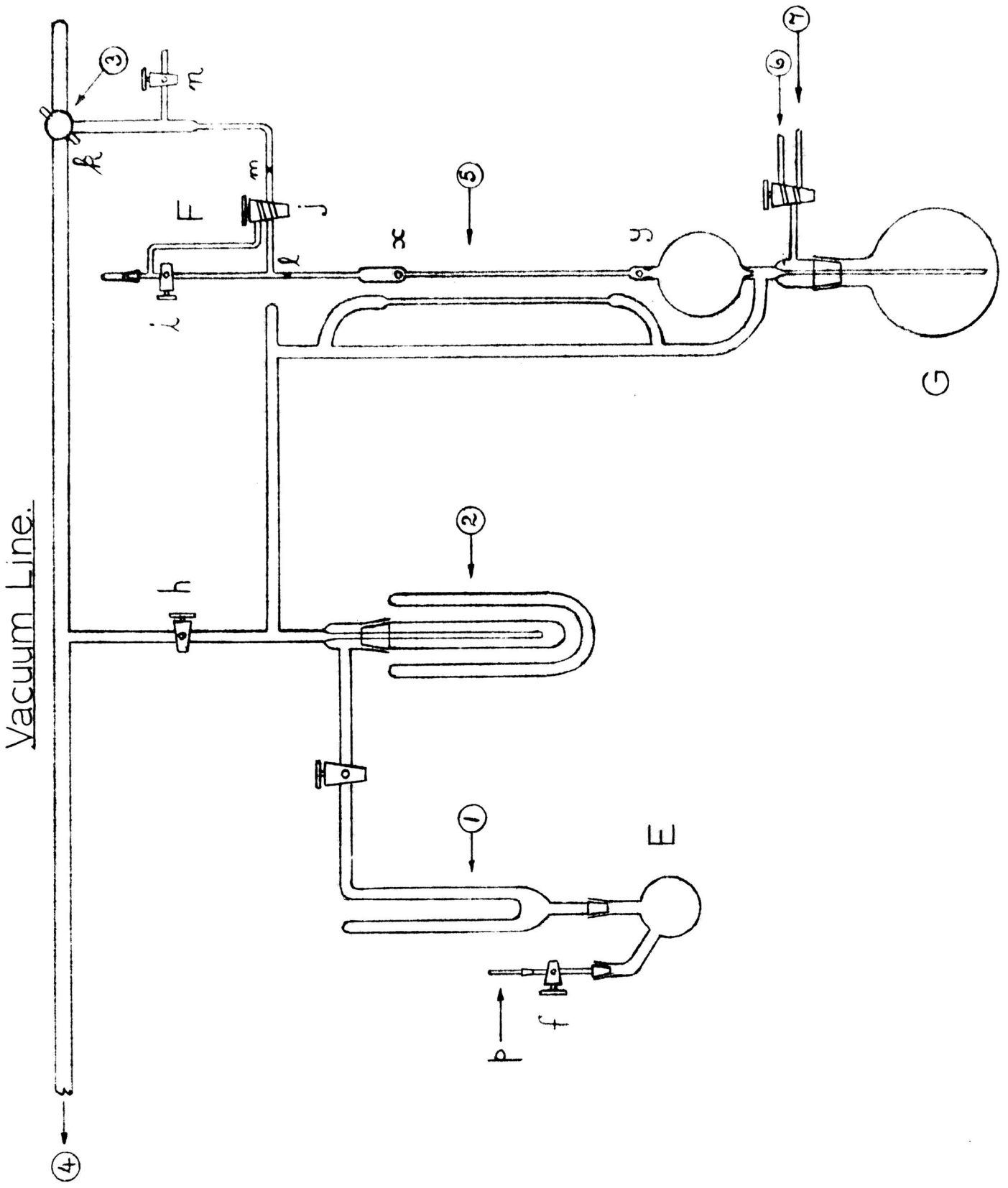
The apparatus shown diagrammatically in Figure 7 was evacuated with a mercury diffusion pump backed by a rotary oil pump. With the exception of the valves x and y, the construction of the system is evident from the diagram. Each valve was made from a $\frac{1}{4}$" diameter corrosion resistant steel ball bearing, (supplied by the Hoffmann Manufacturing Co. Ltd.) which could be firmly held against a ground glass seat with the aid of a magnet. The valve seats were ground using an identical ball bearing and a No.220 silicon carbide abrasive. The best results were achieved with an initial grinding just sufficient to produce a concentric surface around the edge of the given orifice. This surface was then polished with a very fine carborundum paste. Such valves when held in position under a level of mercury formed

Figure 7

Vacuum Line

1	Cold finger trap. Solid CO_2.
2	Slurry of acetone and solid CO_2. Temperature = -78°C.
3	B14 socket and cone.
4	To high vacuum.
5	Capillary tube, cross sectional area = 1.38×10^{-2} $cm.^2$
6	Air or oxygen inlet.
7	To rotary oil pump.
E	50 ml. flask.
F	Sample collecting vessel.
G	McLeod Gauge and Toepler pump.
x and y	Pressure and non-return valves.

Figure 7



an efficient vacuum tight seal. The lower valve y was operated by the solenoids of two 200 ohm post office relays wired in parallel and connected to a 150 volt A.C. supply. An Eclipse Major magnet fitted with modified pole pieces controlled valve x so that pressure and volume measurements could be readily performed. With the capillary tube (5) (cross sectional area = $1.38 \times 10^{-2} cm^2$) the maximum pressure head of 21 cms. corresponded to a volume of 7.47×10^{-2} ml. at N.T.P.

(b) Gas Chromatography Apparatus

The basic apparatus is shown schematically in Figure 8. Where possible this was of a glass construction and all ground joints and taps were lightly greased and held firmly in position. Manganese Oxide in trap 5 efficiently removed traces of oxygen from the carrier gas stream and was readily prepared by passing a slow current of hydrogen over heated manganese dioxide. The glass wool in trap 6 prevented the contamination of the reference pair of elements in the detector cell with manganese oxide. In the absence of such a filter an increase of about 20% was observed in the resistance of these filaments and this necessitated their replacement.

(c) The column and its assembly

A U column, the open ends of which terminated in B5 sockets was made from 10 feet of 5 mm. pyrex glass tubing. This was packed with 40-50 mesh, type 5A Union Carbide molecular sieve, and the ends of each limb lightly plugged with glass wool. A heating mantle was constructed from a

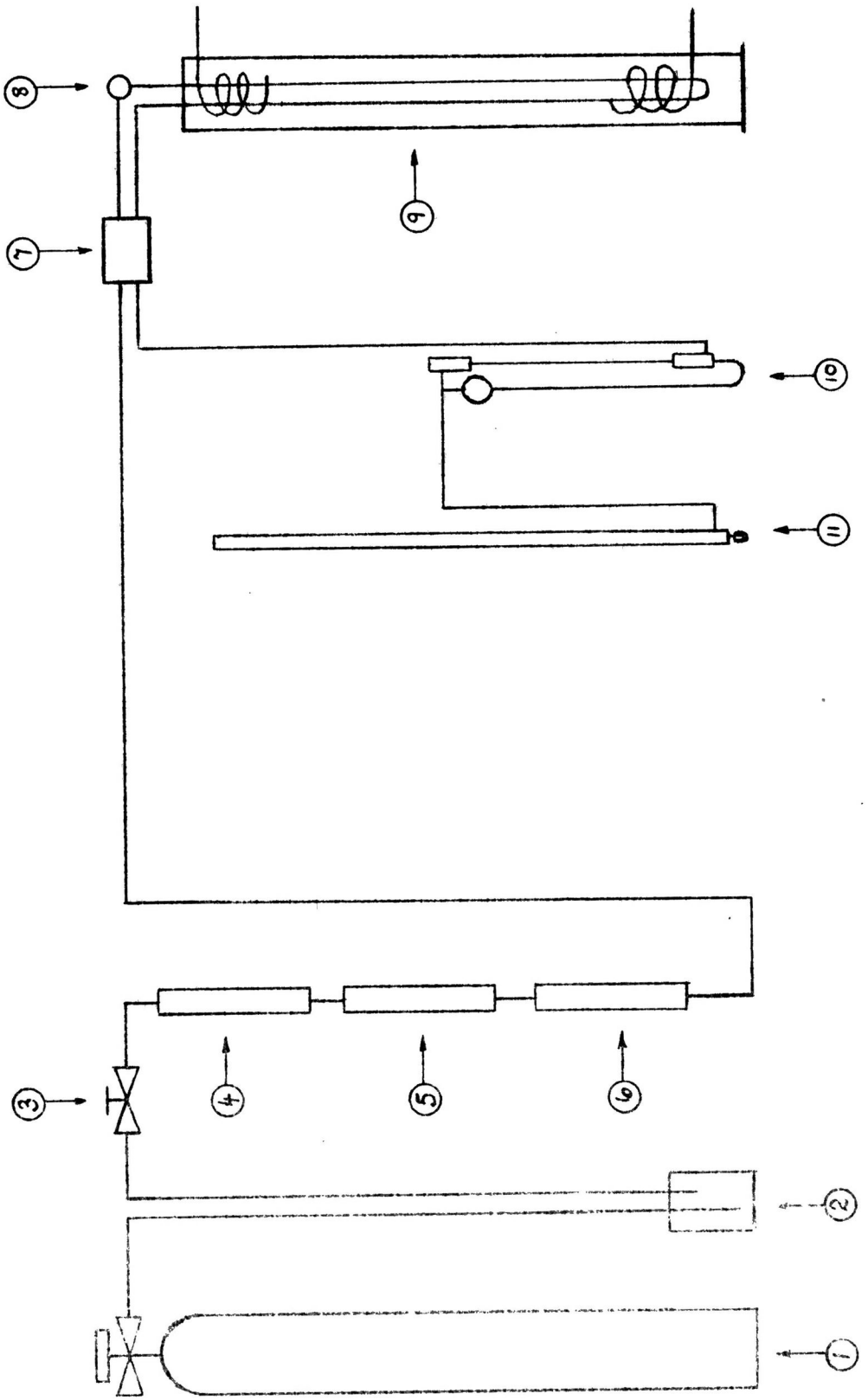
Figure 8

Basic Gas Chromatography Apparatus

1	Carrier gas. Helium or Argon.
2	Surge chamber; 5 litre vessel.
3	Needle Valve.
4	$CaCl_2$ drying tube.
5	Manganese oxide trap.
6	Glass wool trap.
7	Hot wire detector.
8	Sample inlet.
9	Column and heating mantle.
10	Capillary flow meter.
11	Soap film meter.

Figure 8

Basic Gas Chromatography Apparatus.



5 ft. length of 30 mm. diameter pyrex glass tubing wound with 80/20 Vacrom resistance wire to a total resistance of 88 ohms. A paste of fused alumina cement (S11800 ILBTRI-MOR No.913) baked on to this mantle firmly fixed the windings in position. The column was then placed centrally within this mantle and the whole assembly mounted inside a 5" diameter asbestos pipe packed with fused alumina insulation. A Chromel-Alumel thermo-couple (fitted within the limbs of the column and situated at the mid point of the heating mantle) permitted the temperature regulation of the column and was monitored by connection to a previously calibrated milliammeter. The column was then attached to the apparatus (see Figure 9) and the molecular sieve activated prior to use by heating under vacuum to approximately 350°C for about 14 hours. At this temperature a variation of about 30°C was detected along the length of the column.

(d) Detector and Recording Equipment

The detector used throughout was a Gow-Mac four element Pretzel thermal conductivity cell. This was maintained at room temperature for all analyses. A Sunvic recording potentiometer (type RSP 2.) measured the potential developed by the bridge. This instrument was however unsuitable for the successful determination of hydrogen and was replaced in these analyses by a Sefram Graphispot recorder. The circuit diagram is shown in Figure 10.

(e) Standard extraction procedure for dissolved gases

The vacuum line described in section 5(a) was evacuated until a pressure of less than 10^{-5} mm. was indicated by the

Figure 9

Gas Chromatography: Sample Introduction

F	Sample vessel.
1	Column.
2	To hot wire detector. (sample side)
3	From hot wire detector. (reference side)

Figure 9

Gas Chromatography: Sample Introduction.

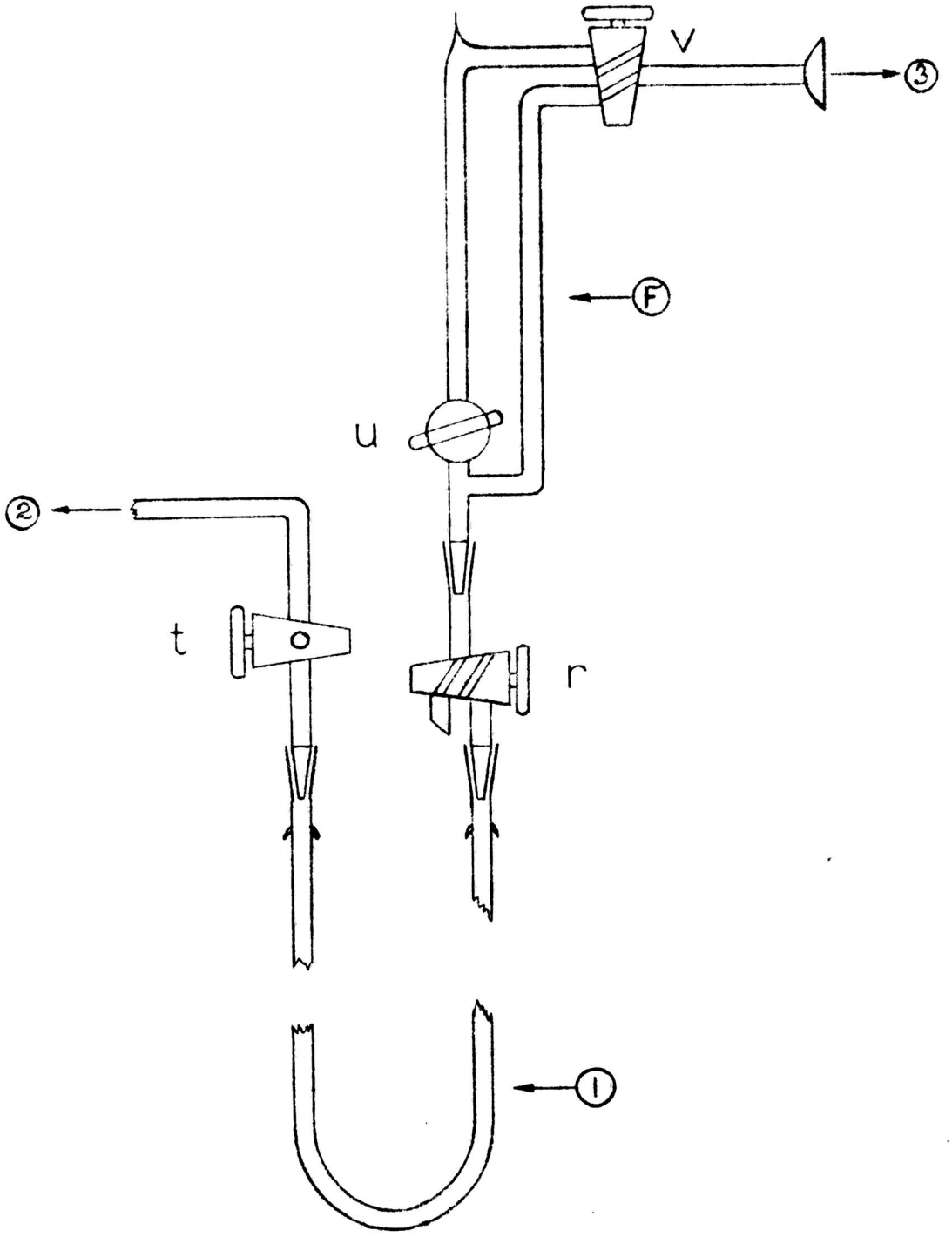


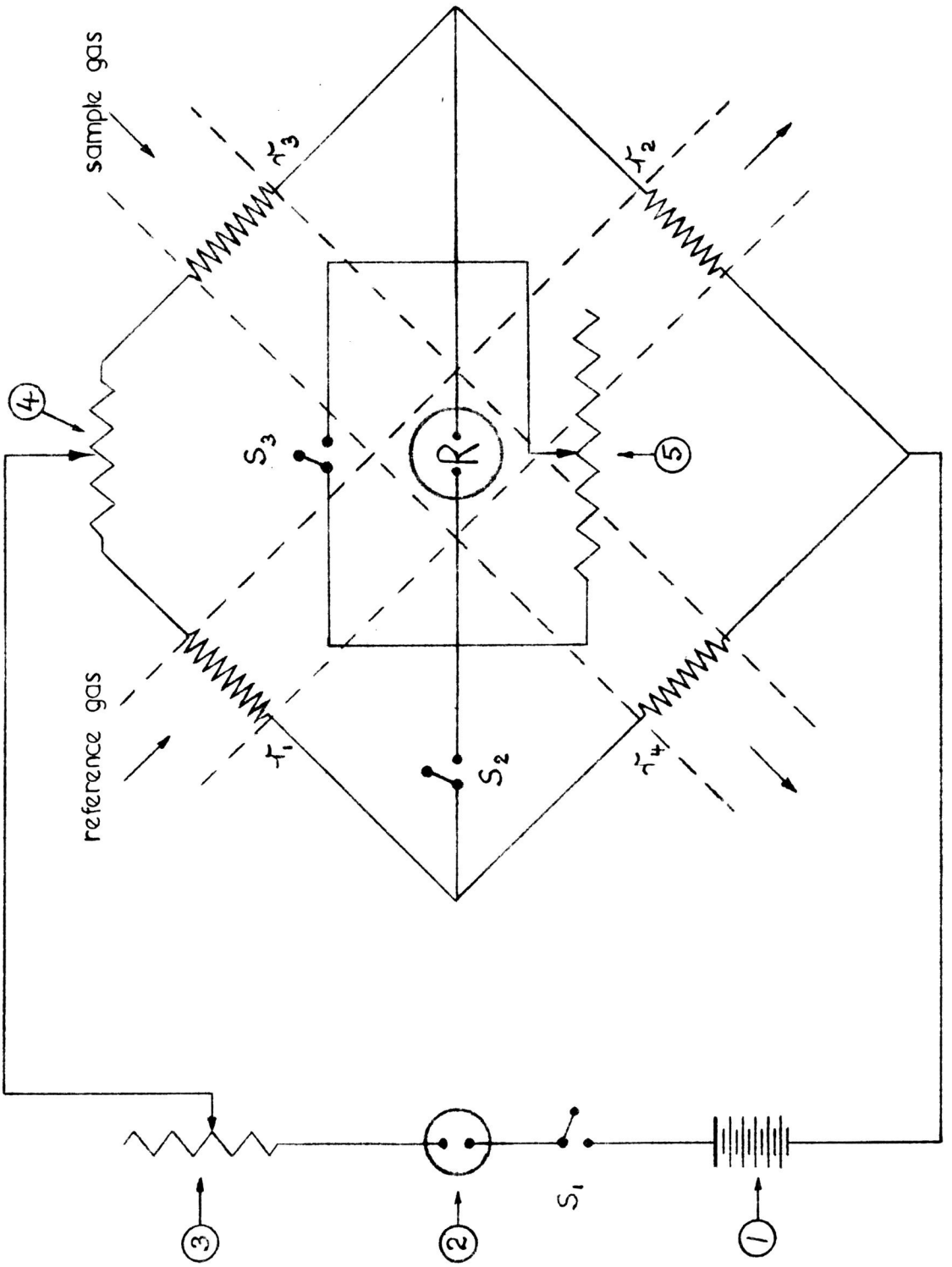
Figure 10

Gas Chromatography: Circuit Diagram

1	6V or 12V Batteries.	
2	500 mA Westinghouse D.C. milliammeter.	
3	25 ohm potentiometer for main current control.	
4	1 ohm helical potentiometer for bridge zero control.	
5	100 ohm Muirhead switched resistance.	
r_1, r_2	Reference detector elements	20 ohms when cold.
r_3, r_4	Sample detector elements	20 ohms when cold.
S_1	Main circuit swith.	
S_2	Switch to short circuit the bridge.	
S_3	Switch to short circuit recorder.	
R	Recorder. Sunvic type RSP2 or Graphispot (type GR4 VAD).	

Figure 10

Gas Chromatography: Circuit Diagram.



McLeod gauge. Tap f was then closed and the B5 plug p removed. The socket was then filled with solution ejected from a syringe prior to its connection at this point. Approximately 1 ml. of the sample was then admitted to vessel E, and the evolved gases exhausted and discarded by successive cycles of boiling, freezing and pumping on the liquid. Taps h, i, j and k were then closed and an aliquot of the solution admitted to E. The dissolved gases were then completely exhausted as above but with transfer of the gas to the capillary tube, (5), by the Toepler pump G. Operation of the valve y after each cycle prevented the back return of the gas into the system. The gas was finally transferred to the L limb of the sample vessel F by raising the mercury level to the constriction l. With tap n open, the sample vessel was then detached by sealing off first at m, and then at l. On lowering the mercury level both valves were operated so that a new sample vessel could be readily sealed at l, without admitting air to the remainder of the system.

(f) Determination of Nitrous Oxide and the separation of Oxygen, Nitrogen and Nitric Oxide by Gas Chromatography.

Helium at a cylinder pressure of 10 lb. per sq. inch and a flow rate of 50 ml. per minute was used throughout as the carrier gas. The detector was operated with a bridge current of 340 milliamps (mA) and the peaks recorded at a chart speed of 30 ins. per hour. The best compromise between baseline stability and maximum sensitivity was achieved with a resistance of 40 ohms in parallel with the

0.5 millivolt (mV) range of the recorder. A full scale deflection under these conditions was therefore equivalent to 1.25 mV. Samples were analysed in the following manner. With carrier gas flowing through the system, vessel F was attached to the column as shown in Figure 9. The side limb was swept free of air and the helium admitted to the column by rotating tap r. When steady zero conditions were obtained the sample was swept into the column by rotating the taps u and v, this latter operation occupying some 3 to 4 seconds. After completing an analysis the taps r and t were then closed to prevent the access of air to the column. The elution times at room temperature for the various gases are given in Table 5.

TABLE 5

Gas.	Elution time (minutes)
H_2	approximately 1 *
O_2	3
N_2	8
NO	14
N_2O	greater than 3 hours

* Sensitivity very poor

Nitrous oxide was not readily eluted under these conditions but a complete separation could be achieved by programming the column temperature. After the elution of the nitric oxide, the temperature of the column was raised within 20 minutes to approximately 150°C using an input of 180 volts to the heating mantle. This temperature was maintained

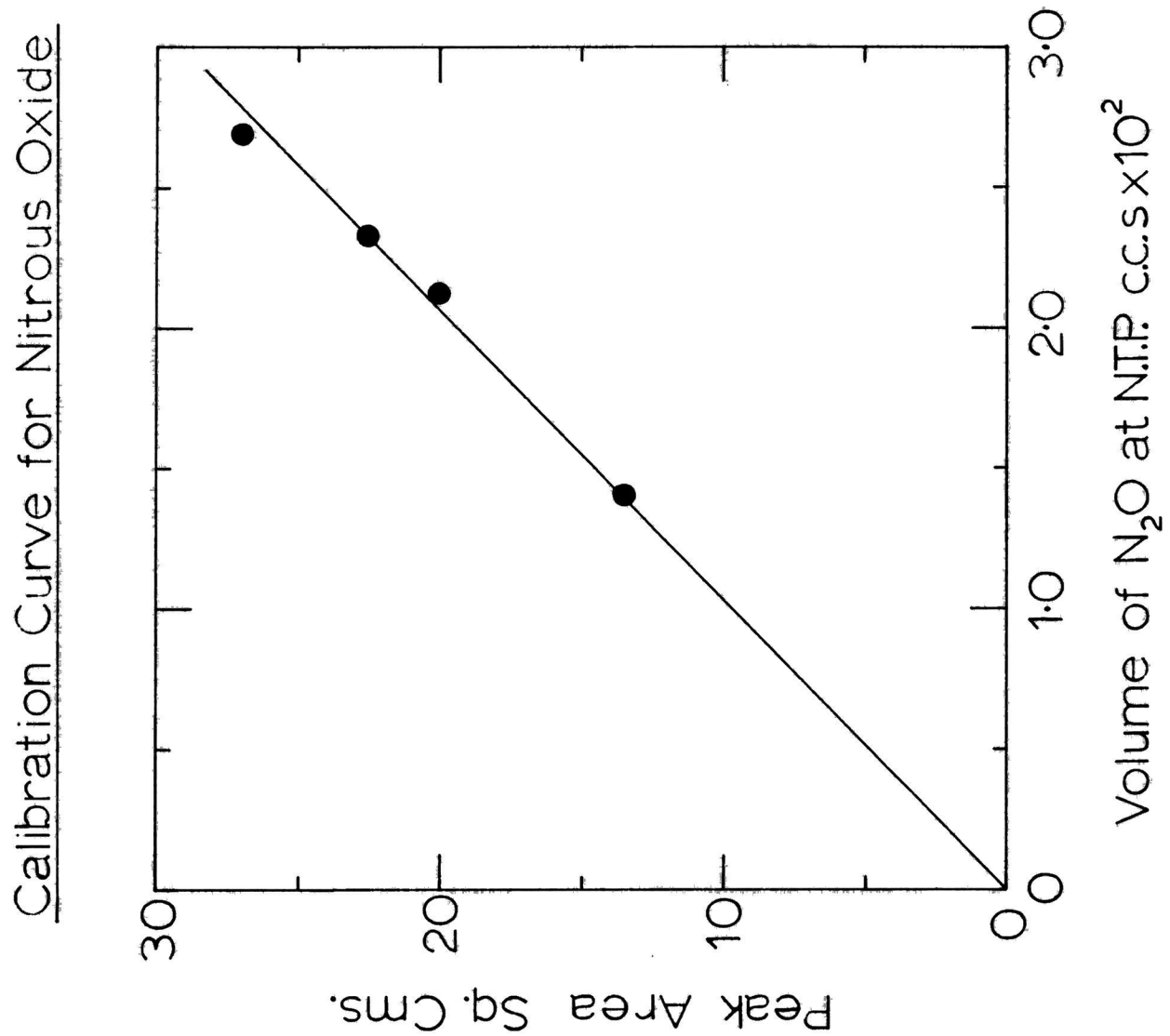
constant for a further 20 minutes (input of 130 volts) after which time the nitrous oxide was eluted. Such a procedure was however restricted in its application by the somewhat inaccurate method of temperature control from day to day, difficulties with the precise control of carrier gas flow rate, and the time required to cool the column prior to the next analysis. Determinations of nitrous oxide were therefore carried out with the column maintained throughout at a constant temperature of about 150°C. Under such conditions the remaining gases were eluted but not separated within 2 to 3 minutes while the elution time for nitrous oxide was reduced to 29 minutes.

The quantitative interpretation of the chromatogram was inferred from separate calibration experiments interspersed with the experimental analyses. Volumes of nitrous oxide used for this purpose were measured on the McLeod gauge after their extraction from aqueous saturated solutions. A typical plot of the recorder peak area as a function of the volume of nitrous oxide is shown in Figure 11. The sensitivity inferred from this slope was 21.7 cm^2 per micromole so that 0.25 micromoles of nitrous oxide could be analysed readily. Errors in these calibrations were approximately $\pm$ 3%.

(g) Determination of Hydrogen

Preliminary experiments with a bridge current of 140 mA and Argon as the carrier gas indicated that hydrogen could be readily detected using the above apparatus. However as a consequence of the sampling procedure, the irregularities

Figure 11


Calibration Curve for Nitrous Oxide
Peak Area Sq. Cms.
30
20
10
0
0
1·0
2·0
3·0
Volume of N_2O at N.T.P. c.c.s x 10^2

induced in the gas flow rate and concomitant variations in the recorder zero were not stabilised within the 1 minute required for the elution of hydrogen. Further experiments designed to overcome this difficulty by extending the elution time included modifications in the mesh size of the molecular sieve, gas flow rate, column temperature and column length. These are summarised in Table 6.

TABLE 6

Experiment	Column length	Column Temp. (°C)	Flow rate mls/min.	Mesh Size	Elution time (mins.)
a	5' spiral	-78	50	60-80	1
b	18' (two U sections)	20	25	80	4
c	10' U	20	30	80	1.75

Method (b) was difficult experimentally because of the high pressure difference across the column and therefore (c) was adopted. The Sunvic instrument was however unsatisfactory for the quantitative recording of the detector signal, only very narrow peaks being obtained with the maximum chart speed of 45 ins. per hour. Using a Sefram Graphispot recorder (type GR4 VAD, kindly loaned by Dr. A.F. Brown) with a full scale deflection of 1 mV and a chart speed of 30 cms. per minute, very satisfactory chromatograms were obtained. Owing to experimental difficulties an absolute calibration of the sensitivity was not carried out as in the case of nitrous oxide. However, chromatograms obtained with the hydrogen

produced on the irradiation of aerated 10^{-3}M potassium bromide solutions were interspersed with experimental analyses. Knowing G_{H_2} in such solutions the concentration of hydrogen was inferred for any given dose (see chapter IV). The results of two such calibrations are given in Table 7, and a photocopy of the chromatogram obtained in experiment (i) is shown in Figure 12. The sensitivity deduced by this method was 124.4 cm^2 per 0.1 micromole. Thus 0.01 micromole of hydrogen could be analysed very readily and this could certainly be extended to 0.005 micromoles.

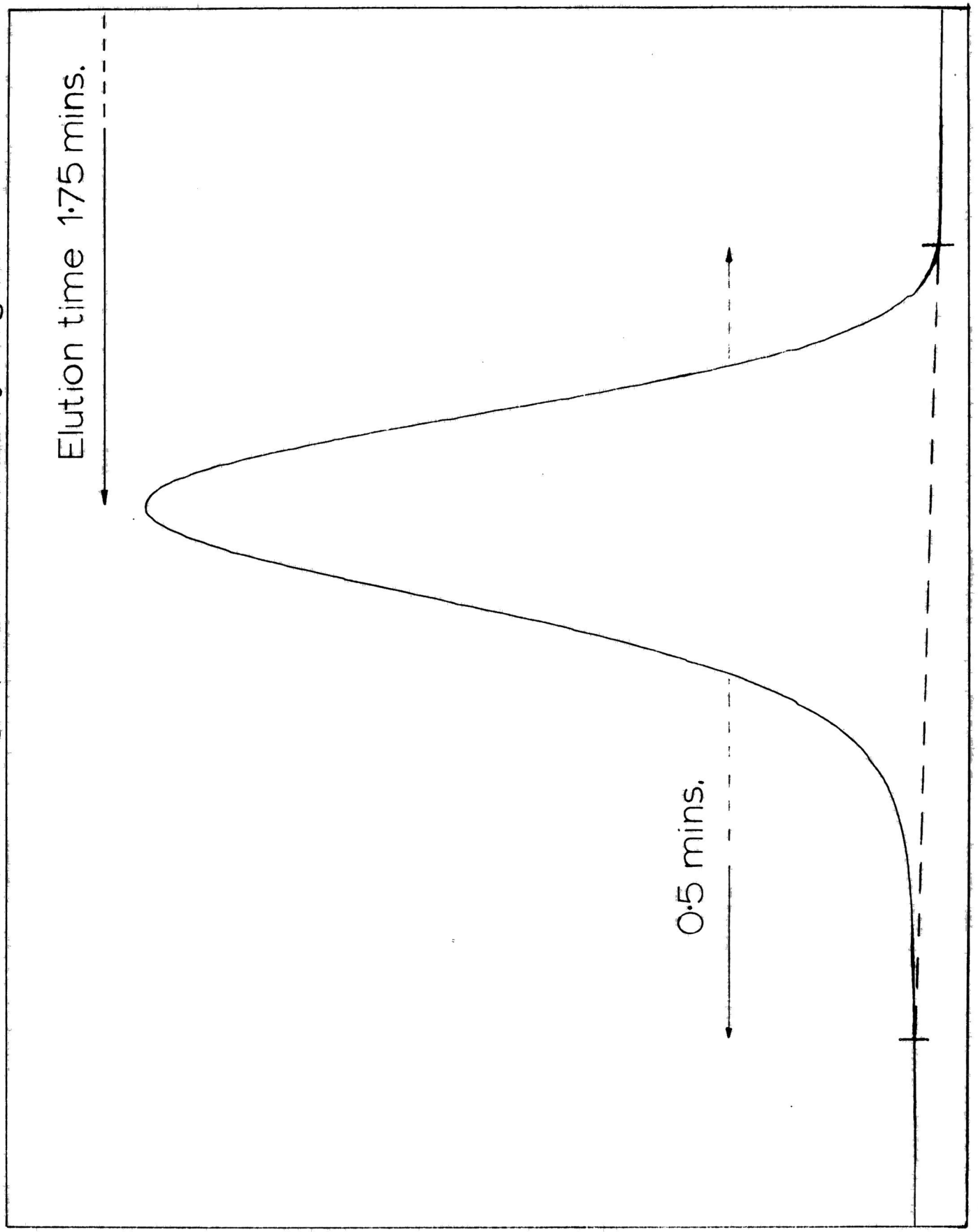
TABLE 7

The production of Hydrogen from irradiated 10^{-3}M Potassium Bromide solutions.

Experiment	Dose ev/l x 10^{-21}	Volume of solution used for analysis (mls.)	Peak Height (cms./ml.)	Peak Area (cms^2/ml.)	Concentration of Hydrogen* (x 10^{-6}M)	Ratio $\frac{\text{Peak Area}}{\text{Peak Height}}$ (cms.)
(i)	1.45	5	2.94	13.16	10.47	4.47
(ii)	3.05	3	6.16_6	27.36	22.0	4.43

* Calculated on the basis G_{H_2} = 0.435 in aerated 10^{-3}M KBr.

Figure 12


Gas Chromatographic Peak for Hydrogen.
Elution time 1·75 mins.
0·5 mins.

CHAPTER IV

RESULTS AND DISCUSSION OF THE γ RADIOLYSIS OF NITRIC OXIDE IN AQUEOUS SOLUTION

Chapter IV

Results.

Solutions of Nitric Oxide in Water

(1) Pure water at natural pH.

Syringes containing 15 ml. aliquots of nitric oxide solutions at their natural pH (approximately 5: see below) were irradiated for different periods with γ rays using the Co^{60} source and irradiation assembly described previously. Concentrations of nitric oxide ranged from 1.26 to 1.93 x 10^{-3}M and it was found that as nitric oxide was consumed, nitrite and nitrous oxide were produced. The water decomposition products, hydrogen peroxide and hydrogen were also obtained. The quantity of nitric oxide consumed and the amount of product detected was expressed in micromoles per litre, (μM/l) as a function of the absorbed dose in electron volts per litre, (eV/l). Figure 13 shows the disappearance of nitric oxide (curve A) along with the production of nitrite, (curve B), while Figure 14 shows the corresponding formation of nitrous oxide (curve C) and hydrogen peroxide (curve D). The various yields of these reaction products were subsequently determined from the initial slope of the respective dose - concentration curves. These are represented by placing the formula in parentheses after the symbol G. It was found that $G_{(-NO)} = 12.0 \pm 0.8$ molecules per 100 eV, $G_{(NO_2^-)} = 5.9_5 \pm 0.2$, $G_{(N_2O)} = 3.1 \pm 0.1_5$ and $G_{(H_2O_2)} = 0.52 \pm 0.05$.

It was apparent from the results obtained for the consumption of nitric oxide and the production of nitrite that the rate of the reaction slowly decreased upon greater than

Figure 13

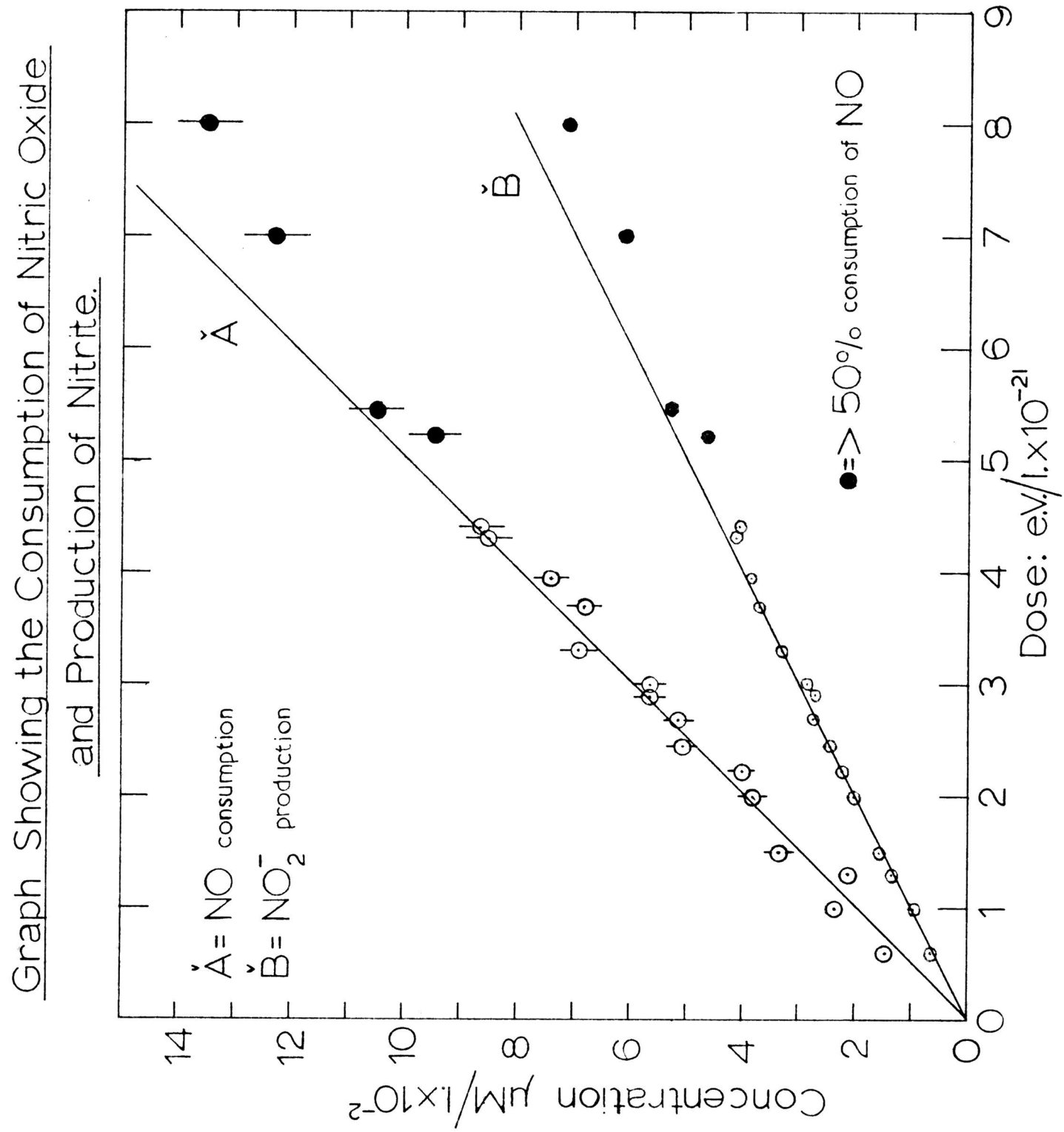
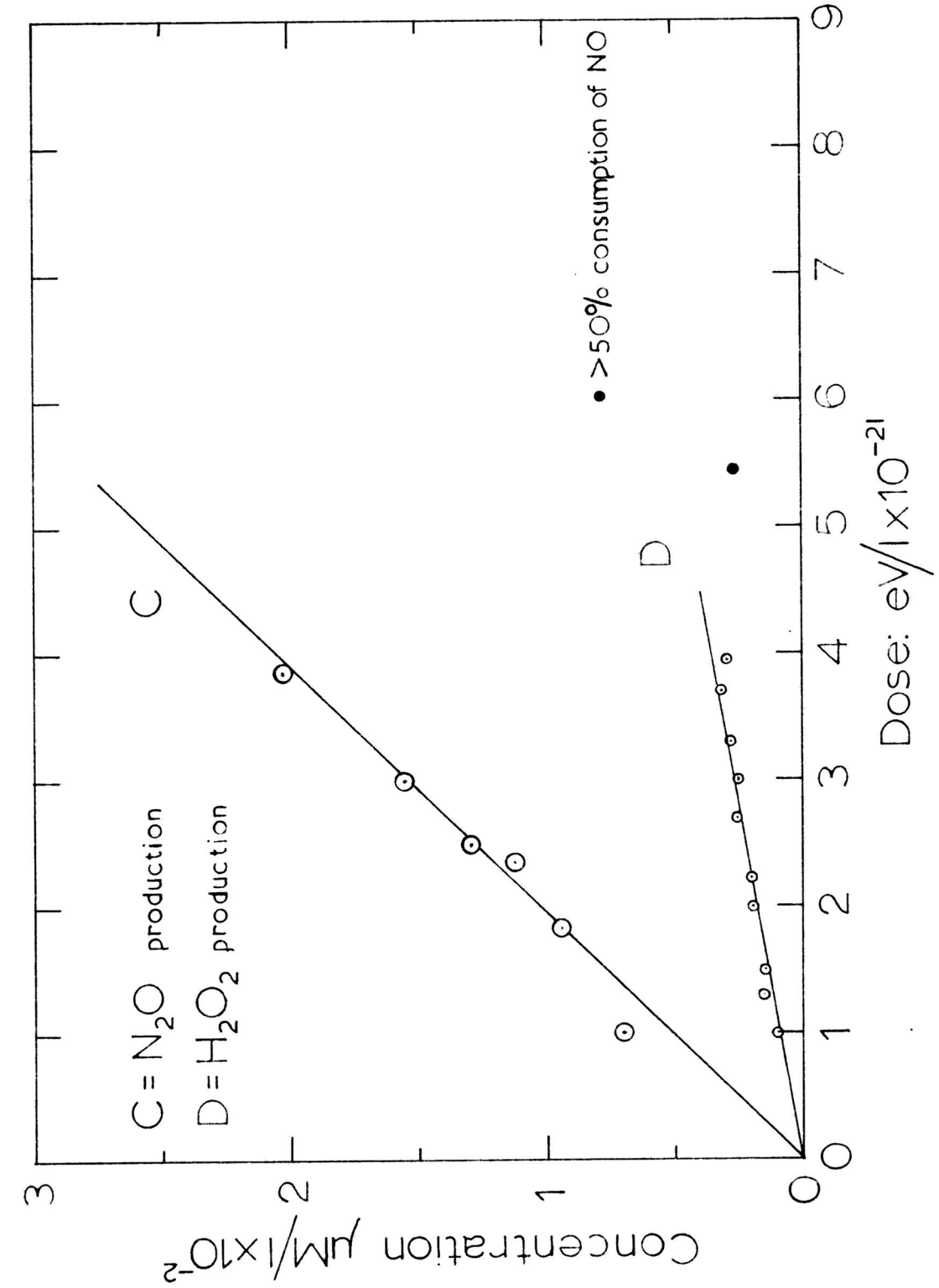

Graph Showing the Consumption of Nitric Oxide and Production of Nitrite.
A = NO consumption
B = NO2- production
A
B
=> 50% consumption of NO
Concentration μM/l.x10-2
Dose: eV./l.x10-21
0
2
4
6
8
10
12
14
1
3
5
7
9

Figure 14

Graph Showing the Production of Nitrous Oxide and Hydrogen Peroxide



about 50% of the nitric oxide being consumed. A complete reaction curve was therefore determined for nitric oxide consumption and nitrite production within a restricted concentration range of nitric oxide from 1.90 to 1.93 x 10^{-3}M. The results together with the corresponding production of hydrogen peroxide are shown in Figure 15. These curves as before are designated by A, B and D, respectively, a notation which for convenience is used throughout the remainder of this thesis.

Nitrogen was not observed as an initial product and nitrate was only detected when all the nitric oxide had been consumed.

The hydrogen yield:

To obtain a value for the hydrogen yield a method of comparison with irradiated bromide solutions was adopted (this has previously been outlined in chapter III 5(g)). The production of hydrogen obtained from solutions of 1.91 and 2.03 x 10^{-3}M nitric oxide was expressed in terms of the recorder peak area (in cms^2 per ml. of irradiated solution) as a function of dose. These values were then compared directly with those obtained for the hydrogen produced on the irradiation of aerated, 10^{-3}M, solutions of potassium bromide. The results are shown in Figure 16. The magnitude of G_{H_2} in aerated bromide solutions was estimated from the data of Hochanadel and Ghormley,[39] by plotting G_{H_2} as a function of the cube root of the oxygen concentration in oxygenated and deaerated bromide solutions (Figure 17). The interpolated value $G_{(H_2)}^{Br^-(aerated)} = 0.435$, and from the ratio of the two

Figure 15

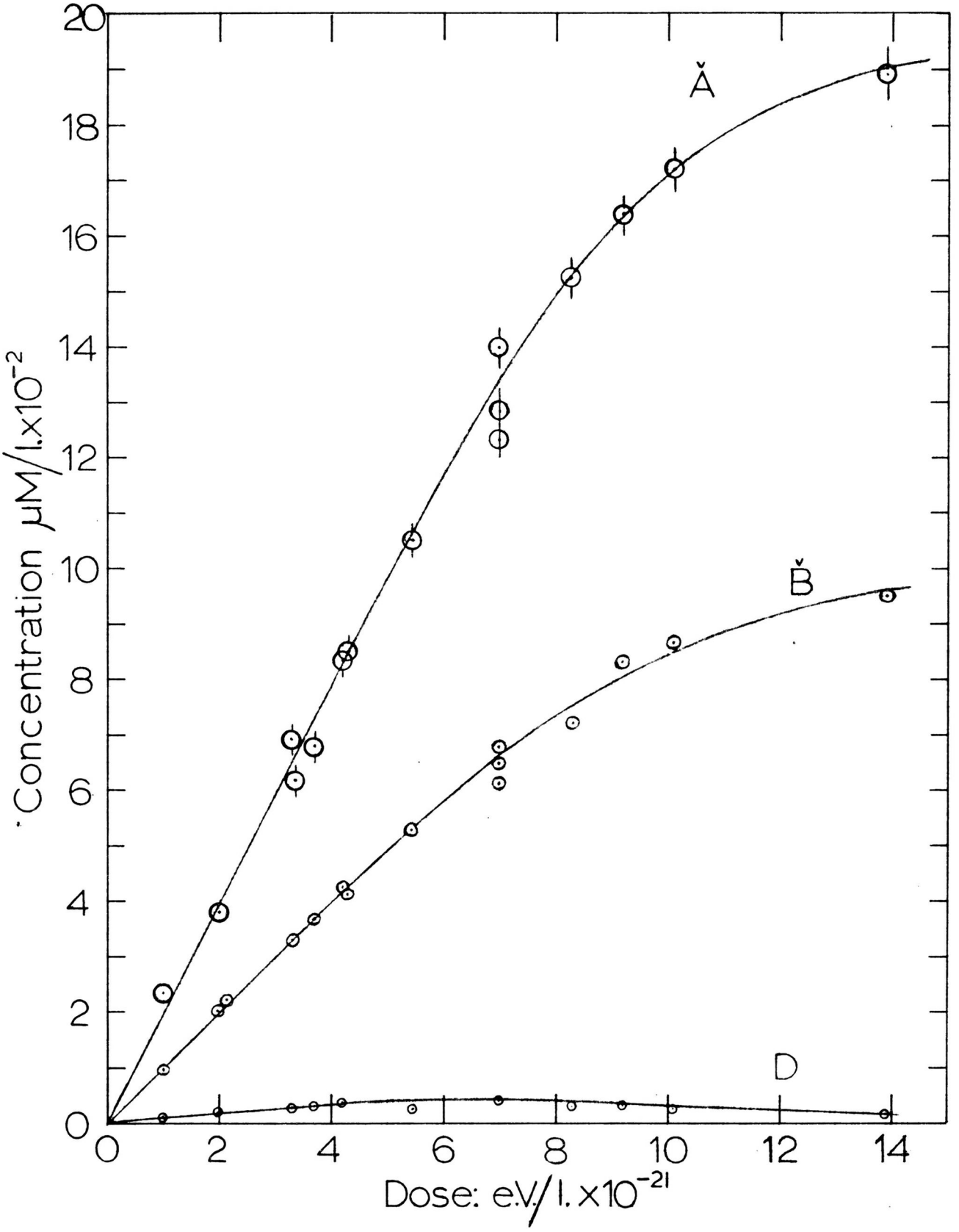

Concentration μM/l.x10⁻²
Dose: e.V./l. x10⁻²¹
Ă
B̆
D
0
2
4
6
8
10
12
14
16
18
20

Figure 16

Graph Showing the Production of Hydrogen from Nitric Oxide and Bromide Solutions

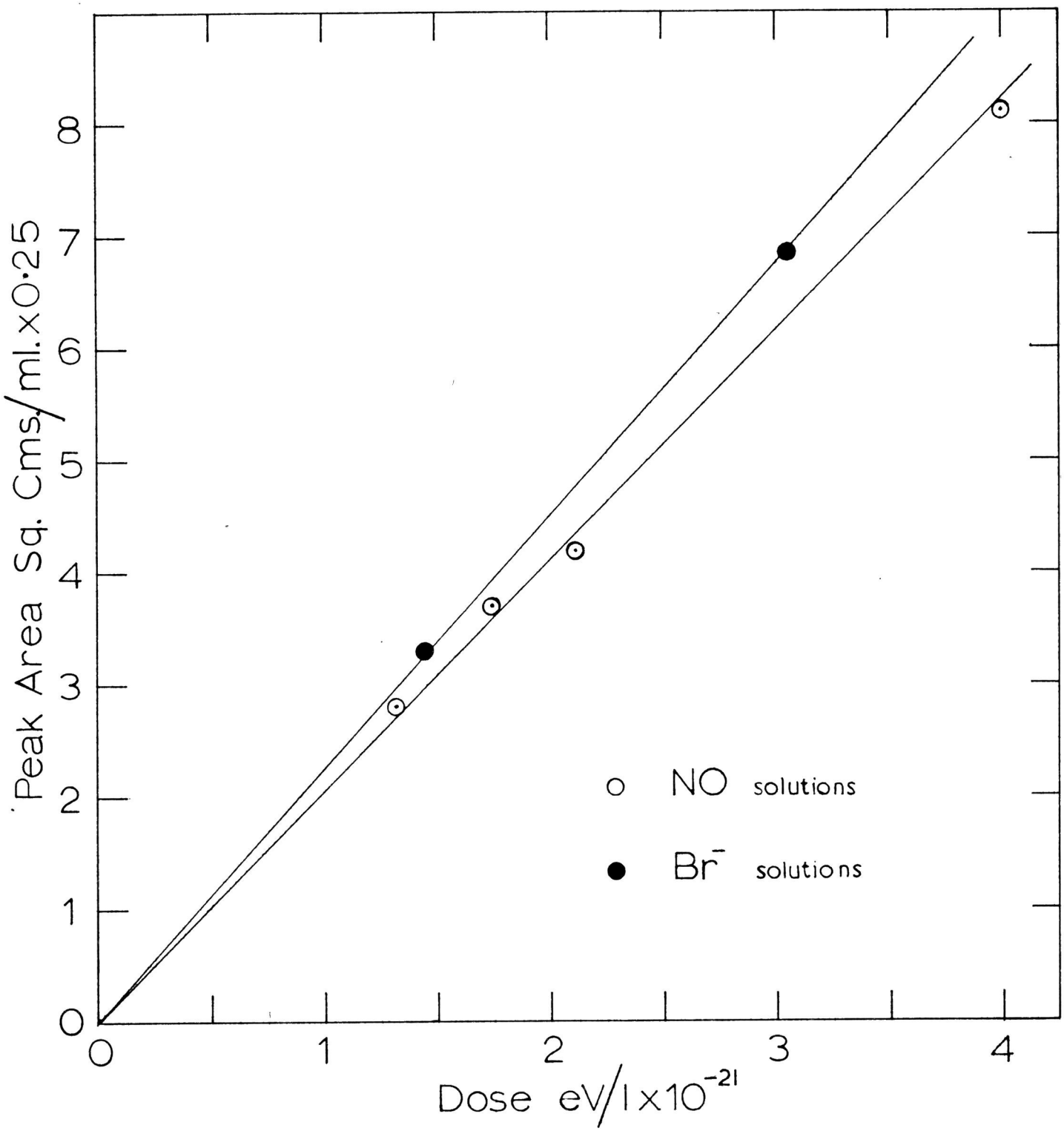
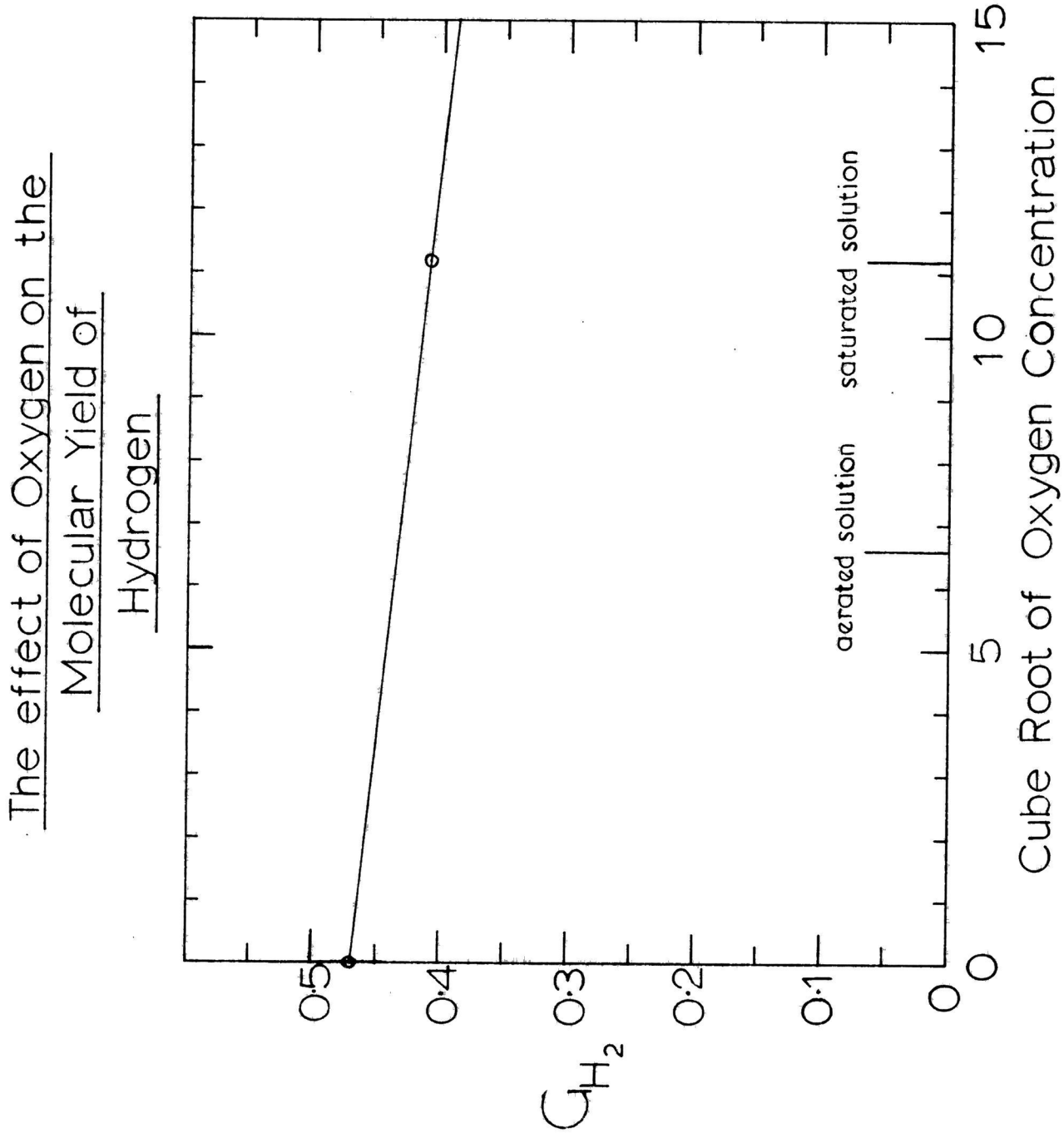


Figure 17


The effect of Oxygen on the Molecular Yield of Hydrogen
G_{H_2}
0·5
0·4
0·3
0·2
0·1
0
0
5
10
15
Cube Root of Oxygen Concentration
$\times 10^2$
aerated solution
saturated solution

slopes in Figure 16 a value of $G_{(H_2)} = 0.395$, taken to be 0.40, was deduced for the nitric oxide solutions.

The pH of nitric oxide solutions:

As nitric oxide solutions are readily oxidised in air to form nitrous acid, a precise determination of the initial pH of such solutions was not possible. The pH of a fully oxidised solution was measured as 3.0, and this value corresponds to that expected for about 2×10^{-3} M HNO_2. Since the pH of distilled water and purified water were measured as 5.4 and 6.0, respectively, it was assumed that the initial pH of the nitric oxide solutions would be in this region. However, on irradiation, the concentration of nitrite (present as partially dissociated nitrous acid) increases with dose, and a progressive decrease in the pH of the solution is to be expected. The calculated pH of such solutions using the dissociation constant of $HNO_2 = 4.6 \times 10^{-4}$ at 25°C[40] are shown in Table 8

TABLE 8

Concentration of HNO_2 ($\times 10^{-4}$ M)	Degree of Dissociation	Calculated pH
1	0.85	4.07
3	0.69	3.68
4	0.63	3.60
5	0.60	3.52
10	0.49	3.31
20	0.36	3.14

The concentration of HNO_2 produced in the above experiments was generally between 1 and 4×10^{-4}M, so that the final pH

of the solution should be between 3.6 and 4.0. With the maximum possible concentration of HNO_2, the final pH would be no less than 3.3. While this pH does not affect the magnitude of the primary radical yields it may affect the nature of the reducing radical. This latter aspect is important for the interpretation of any competitive kinetic studies and is discussed more fully in chapter V.

(2) The effect of hydrogen peroxide at natural pH.

The molecular yield of hydrogen peroxide $G_{(H_2O_2)} = 0.52$, observed in the above work is below that of the accepted value $G_{H_2O_2} = 0.71$ in neutral water.[4] As this decrease may have arisen as a result of a small amount of a thermal reaction between hydrogen peroxide and nitric oxide, or possibly a radical induced reaction, the following two experiments were undertaken to indicate the importance, if any, of either of these two possibilities. The hydrogen peroxide used in this work was prepared by irradiating purified water at neutral pH.

(1) It was determined that in solutions approximately 1.6×10^{-3}M in nitric oxide and 10^{-4}M in hydrogen peroxide, a slow thermal reaction producing nitrite occurred (Table 9). In such solutions the concentration of nitrite produced was approximately double that of the hydrogen peroxide consumed.

(2) Solutions containing approximately 1 to 1.5×10^{-4}M of hydrogen peroxide and 1.8×10^{-3}M of nitric oxide were irradiated such that no greater than about 50% of the nitric oxide was consumed. Samples were then analysed immediately after irradiation for the production of nitrite, together

TABLE 9

Experiment	Time	Initial Concentration of H_2O_2 ($\times 10^{-6}$M)	Initial Concentration of Nitrite ($\times 10^{-6}$M)	Decrease in H_2O_2 Concentration ($\times 10^{-6}$M)	Increase in Nitrite Concentration ($\times 10^{-6}$M)
1	0 3 days	129 65	3 115	64	112
2	0 18 hours	141 127	3.4 18.0	14	14.6
3	0 18 hours	96 91.5	3.0 16.0	4.5	13.0
4	0 3.5 hours	156 153	1.8 7.5	3	5.7

with the residual nitric oxide and hydrogen peroxide. The consumption of nitric oxide and production of nitrite were found to be linear with dose (Figure 18) and the respective yields determined as $G_{(-NO)} = 12.5 \pm 0.9$, and $G_{(NO_2^-)} = 5.7 \pm 0.2$. The concentrations of hydrogen peroxide and nitrite were also determined at various time intervals following the completion of an irradiation and these results together with the initial measurements are given in Table 10.

Within experimental error the respective yields for $G_{(-NO)}$ and $G_{(NO_2^-)}$ obtained in these experiments are seen to be equivalent to those previously obtained in solutions of nitric oxide alone. Furthermore no marked decrease, but rather a slight increase, was detected in the initial concentration of hydrogen peroxide as a function of dose. However a post irradiation reaction consuming hydrogen peroxide and producing nitrite was observed, the rate of which was significantly faster than that of the pre-irradiation rate found in 2(1) above. A more thorough investigation of this aspect was not undertaken as such a reaction was not detected after the irradiation of solutions of nitric oxide alone.

It would appear therefore that concentrations of hydrogen peroxide less than or equal to about 1.5×10^{-4}M are without significant effect on the reaction mechanism either thermally or via some radical induced reaction.

Figure 18

Nitric Oxide Consumption and Nitrite Production in solutions containing Hydrogen Peroxide.

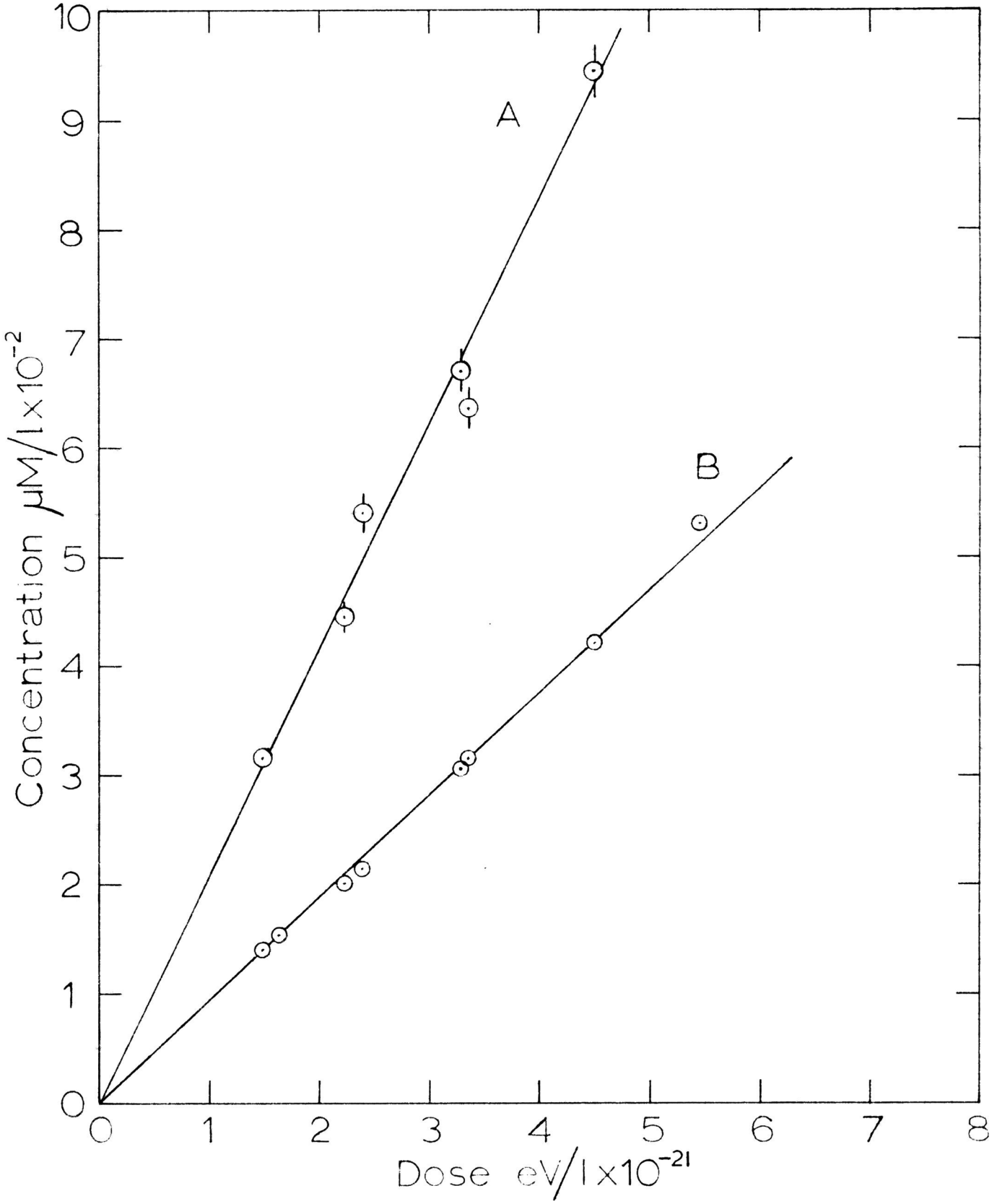


TABLE 10

Initial H_2O_2 Concentration ($\times 10^{-6}$M)	Initial Nitrite Concentration ($\times 10^{-6}$M)	Dose (eV/l $\times 10^{-21}$)	Time after irradiation and removal of nitric oxide	Post Irradiation concentrations ($\times 10^{-6}$M)	
				H_2O_2	Nitrite
127	18	2.38	4 minutes	135	213
			?	127	216
91.5	16	1.63	4 minutes	102	153
		3.27	4 minutes	87	304
			30 minutes	78	?
153	7.5	1.48	4 minutes	159	139
			14 hours	63	192
		2.22	4 minutes	162	199
			35 minutes	154	212
		3.36	4 minutes	161	314
			40 minutes	131	323

(3) The effect of pH

Solutions of nitric oxide of concentrations about 1.60 to 1.90 x 10^{-3}M were prepared in approximately N/100, N/10, and in 0.8N A.R. sulphuric acid. In the former cases the pH of the solution prior to saturating with nitric oxide was measured on a Muirhead pH meter (type D-417-A). The pH of the 0.8N sulphuric acid solution was assumed to be 0.45. Samples were irradiated such that up to approximately 50% of the nitric oxide was consumed, and then analysed for nitrite together with the residual nitric oxide. The consumption of nitric oxide and formation of nitrite were linear with dose at all pH values, and the respective dose - concentration curves are shown in Figures 19 and 20. At pH 0.45 and 1.50, the yields were $G_{(-NO)} = 15.0 \pm 1.0$; $G_{(NO_2^-)} = 6.5 \pm 0.2$, and at pH 2.2, $G_{(-NO)} = 13.2 \pm 0.7$, and $G_{(NO_2^-)} = 6.2 \pm 0.2$.

Two possible sources of error arose in these experiments as a consequence of the lower pH. The first of these was the observed decomposition of the post irradiation nitrite solutions, the capacity of the buffer solution being insufficient on adding the N/10 or 0.8N sulphuric acid solutions (see chapter III (2)). This effect was completely inhibited by including in the buffer solutions the requisite quantity of sodium hydroxide to neutralise the excess acid. Secondly, the nitrite once formed by irradiation might then be progressively decomposed as the irradiation proceeds. To investigate this possibility a number of solutions of nitrite were prepared in N/10 sulphuric acid and the concentration of nitrite, in the presence and absence of both

Figure 19

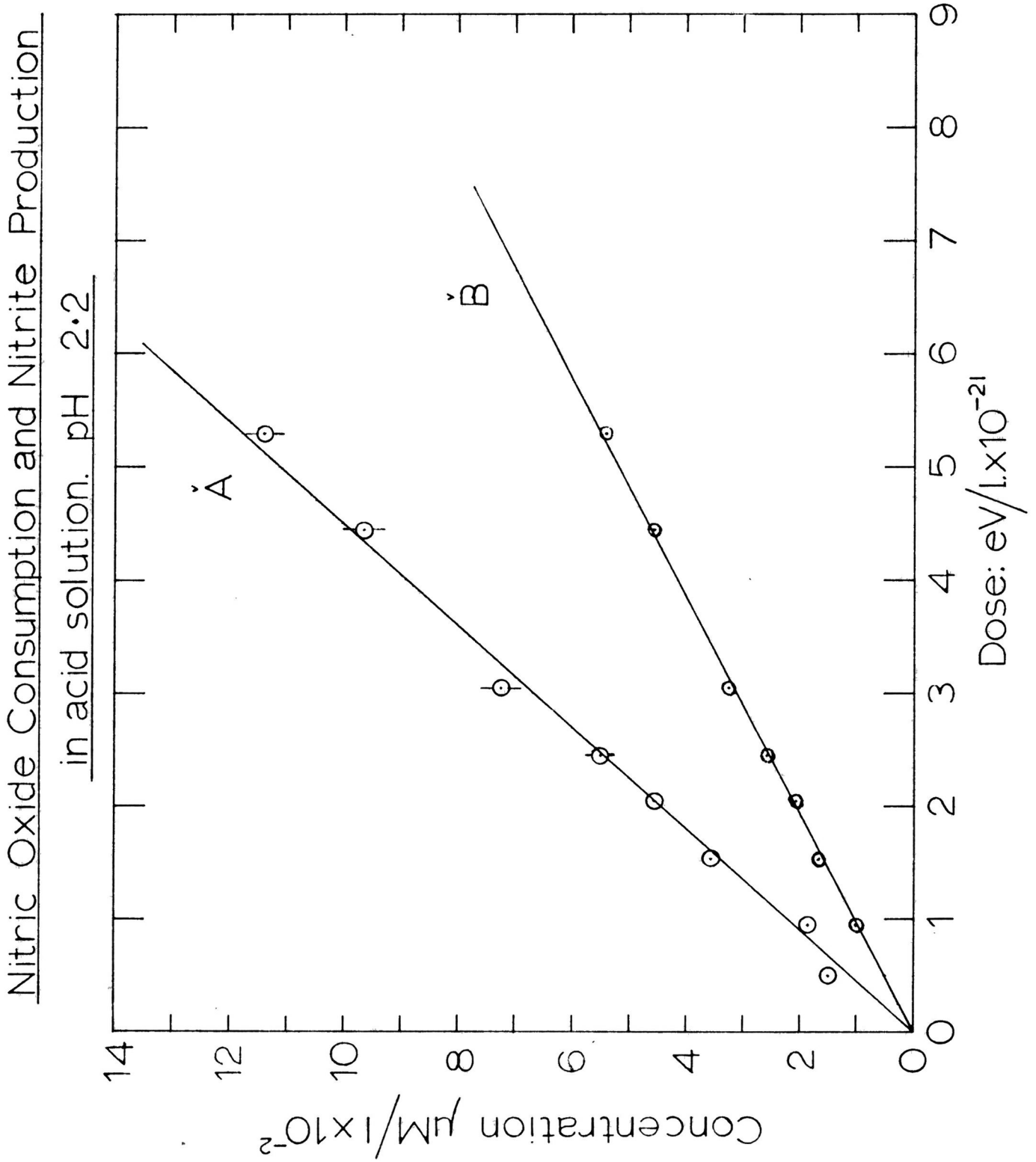
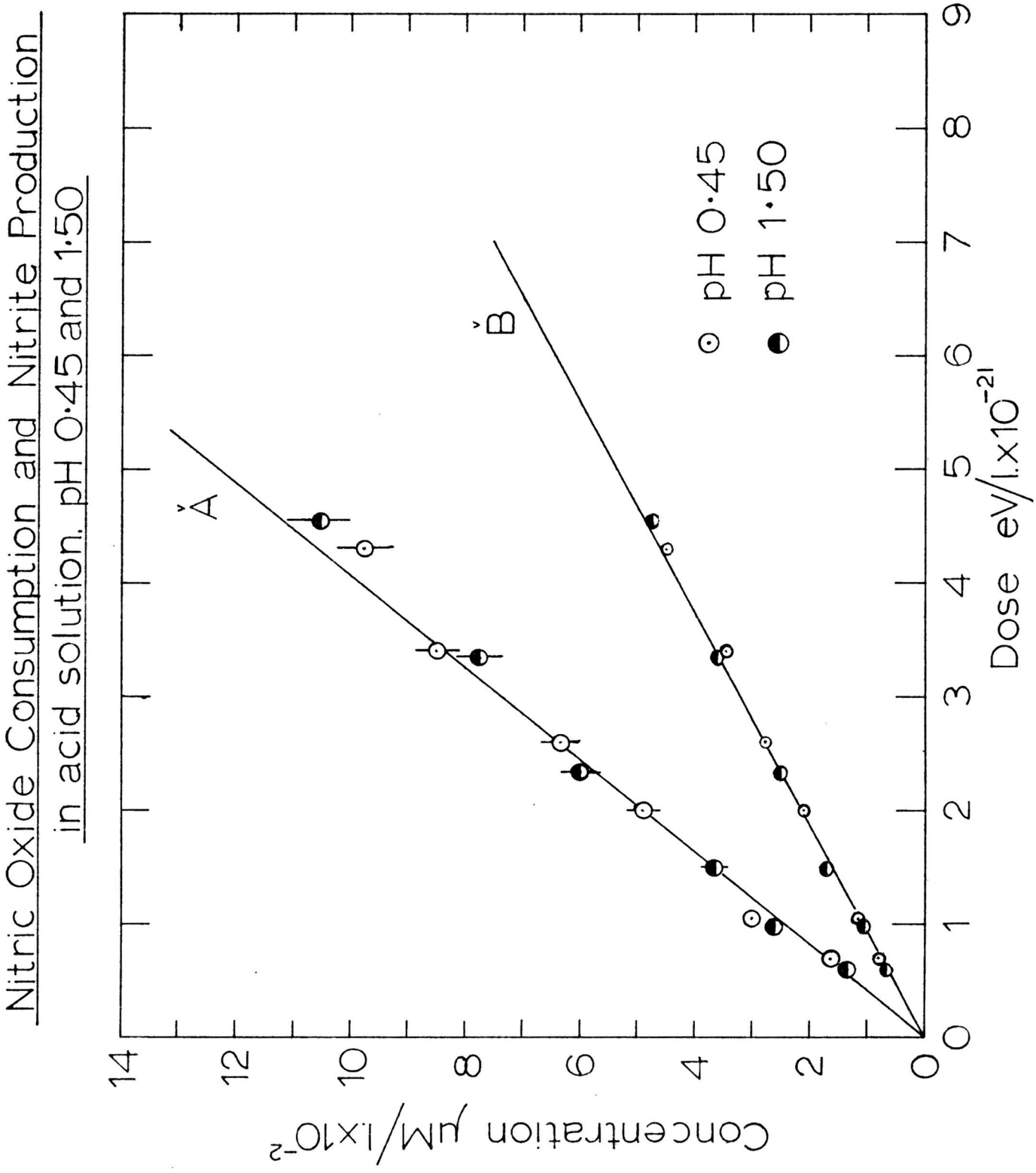

Nitric Oxide Consumption and Nitrite Production
in acid solution. pH 2·2
A
B
Concentration μM/l x10⁻²
Dose: eV/l.x10⁻²¹
0
2
4
6
8
10
12
14
1
3
5
7
9

Figure 20


Nitric Oxide Consumption and Nitrite Production
in acid solution. pH 0·45 and 1·50
Concentration μM/l.x10⁻²
Dose eV/l.x10⁻²¹
pH 0·45
pH 1·50
A
B
0
2
4
6
8
10
12
14
1
3
5
7
9

oxygen and nitric oxide, observed as a function of time. The results obtained are shown in Table 11.

It was evident that nitric oxide prevented the acid decomposition of nitrite ion and therefore the second mentioned possibility would not be a complicating factor in these experiments. The mechanism of this protective effect was not investigated.

(4) Discussion

When dilute aqueous solutions are irradiated the water decomposes to yield the molecules hydrogen and hydrogen peroxide, together with OH radicals and reducing species, generally regarded as H atoms. The nature of this reducing specie is discussed in greater detail in the next chapter but for the present can be regarded as H without affecting the conclusions to be drawn about the reaction mechanism. The overall process of water decomposition can be represented by the equation

$$G_{H_2O} \longrightarrow G_H + G_{OH} + G_{H_2} + G_{H_2O_2}$$

in which G_H and G_{OH} are the numbers of H atoms and OH radicals respectively which are available to react with solutes for each 100 eV of energy deposited in the water. Values appropriate in neutral solution when Co^{60} γ rays are the source of radiation, are $G_H = 2.9$, $G_{OH} = 2.4$, $G_{H_2} = 0.45$ and $G_{H_2O_2} = 0.71$[4]

The yield obtained in this work for the consumption of nitric oxide is considerably greater than those of the primary radical yields and is similar in magnitude to that

TABLE 11

Time (hours)	Concentration of Nitrite ($\times 10^{-4}$M)					
	Aerated Solution (i)	Deaerated Solutions (ii)	(iii)	Solutions containing approximately 1.7×10^{-3}M Nitric Oxide (i)	(ii)	(iii)
0	9.1	15	20			
1		12.4	16.1		12.4	16.1
2				7.37	12.4	16.2
3	7.03					
6						
7						
20	3.29			7.34		
25	2.67			7.44		
100				7.40		

obtained for ferric ion in the ferrous sulphate system. This indicates that some sequence of radical reactions must be taking place. A reaction mechanism consistent with the experimental observations is based on the likely assumption that nitric oxide will react rapidly with both H and OH, thus protecting H_2 and H_2O_2 from radical attack, as in

$$OH + NO = HNO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$H + NO = HNO \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

It is then proposed that the HNO molecule formed in (2) can then undergo further reaction with nitric oxide to produce nitrous oxide and OH

$$HNO + NO = N_2O + OH \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The OH formed in (3) then reacts further according to (1) to produce HNO_2, which at neutral pH is fully dissociated into H^+ and NO_2^-.

This mechanism predicts that

$G_{(-NO)} = 3G_H + G_{OH}$; $G_{(NO_2^-)} = G_H + G_{OH}$ and $G_{(N_2O)} = G_H$

where the parentheses after the letter G denote the observed yield of reaction product in molecules per 100 eV. Substituting the accepted values for G_H and G_{OH} at neutral pH then

$G_{(-NO)calc.} = 11.1$, $G_{(NO_2^-)calc.} = 5.3$ and $G_{(N_2O)calc.} = 2.9$.

The free radical yields are well known to increase with decrease in pH and the values $G_H = 3.7$, and $G_{OH} = 2.9$, are appropriate in 0.8N sulphuric acid solution, while $G_H = 3.3$, and $G_{OH} = 2.7$ at pH 2.2[4]

Substituting these values in the above expressions for

$G_{(-NO)}$ and $G_{(NO_2^-)}$ then at pH 0.45

$$G_{(-NO)calc.} = 14.0, \text{ and } G_{(NO_2^-)calc.} = 6.6$$

and at pH 2.2

$$G_{(-NO)calc.} = 12.6, \text{ and } G_{(NO_2^-)calc.} = 6.0.$$

All the above calculated values are in quite good agreement with experiment and the above mechanism is further supported on consideration of the now well established data concerning the structure and thermochemical properties of the HNO molecule.

The HNO molecule

This molecule has long been postulated as an intermediary in a variety of photochemical and free radical reactions.[41] Smallwood,[42] for example, found that in the gas phase nitric oxide catalysed the recombination of H atoms without itself being reduced.

The reactions

$$H + NO = H — NO$$

$$H — NO + H = H_2 + NO$$

were proposed to account for these observations. More recently it has been postulated as an important intermediary in pyrolytic paraffinic decomposition reactions which are inhibited by nitric oxide.[43,44]

Definite evidence for a compound of this nature was first provided by Harteck.[45] An explosive solid of empirical composition $(HNO)_n$ was obtained by condensing the products of the reaction of H atoms with NO in a liquid air trap placed close to the reaction zone. This product decomposed to give nitrous oxide and water Dalby[46] first identified

HNO spectroscopically during the flash photolysis of nitrated paraffins and mixtures of ammonia and nitric oxide, and confirmed earlier postulates by Hirschlaff and Norrish[47] of its presence in the photochemical decomposition of CH_3NO_2 and $C_2H_5NO_2$. From a consideration of the various spectroscopic parameters he concluded that the molecule was non-linear and of the form H - N = O, thus excluding the possible structure N — O —H. The infra red absorption spectrum[48,49] of HNO, detected during the photolysis of CH_3NO and CH_3NO_2 in the solid phase,[48] confirmed the above observation and indicated an H - N = O bond angle of 110°.

Cashion and Polanyi[50] observed an emission spectrum attributed to excited HNO in the reaction of nitric oxide with H atoms. Assuming zero activation energy for this reaction they set a lower limit of approximately 46 k.cals/mole. for the association of H + NO. Clement and Ramsay[51] in a further study of this spectrum observed that some of the bands showed a distinct breaking off in rotational structure, due to predissociation in the excited state. These results set an upper limit of 48.6 k. cal./mole. for the dissociation energy of the HNO molecule. Further information confirming this predissociation limit and giving more precise values for the geometrical parameters of the HNO molecule has been obtained by Bancroft et al.[52] Clyne and Thrush[53,54] have studied the overall kinetics of the light emission (due to excited HNO) in a considerable extension of Smallwood's work. They showed that the reaction

$$H + NO + M = HNO + M$$

where the third body M = H_2 or inert gas, possessed a small negative activation energy of -0.6 k. cals./mole. The absence of an activation energy for this reaction clearly showed that the dissociation energy of the H — NO bond, D(H — NO), corresponded to the predissociation limit and a value of 48 k. cals./mole. was adopted.

Combining this value with the data presented in Table 12, the thermochemistry of reactions (1), (2) and (3) can be evaluated.

TABLE 12

Thermochemistry of radicals and molecules in reactions (1), (2) and (3)

Specie	Reference Number	k. cals. per mole.		
		Standard Heat of formation (gaseous)	Heat of solution	Heat of formation (aqueous)
H	55	52.1	-1 ± 0.5	51.1
OH	55	8.88 ± 0.5	-7 ± 2.5	2 ± 3
NO	56	21.6	-4.6 *	17
HNO_2	56			-28.4
N_2O	57	19.6	-6.2	13.4

* It was assumed that the solvation energies of HNO and NO were similar to that of other neutral molecules such as oxygen or nitrous oxide. Values of between 4 and 6 k.cals./mole. were adopted.

		ΔH(aq) k. cals. mole^{-1}
(1)	$HO + NO = HNO_2$	-47.4
(2)	$H + NO = HNO$	-48.0
(3)	$HNO + NO = N_2O + OH$	-21.6

Clearly the overall sequence of reactions in energetically favourable, the important reaction (3) being some 20 k. cals. mole^{-1} exothermic.

An Alternative Mechanism

It is of interest at this juncture to consider an alternative mechanism which can be proposed if it is assumed that reaction (1) does not produce nitrite directly, but rather by a sequence of reactions based on the assumption that the intermediary is HONO (i.e. undissociated nitrous acid)

$$H + NO = HNO \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$
$$HO + NO = HONO \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$
$$HONO + NO = NO_2 + HNO \quad \ldots\ldots\ldots\ldots (5)$$
$$NO_2 + NO + H_2O = 2HNO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$
$$HNO + HNO = N_2O + H_2O \quad \ldots\ldots\ldots\ldots (7)$$

This mechanism predicts that

$G_{(-NO)calc.} = 3G_{OH} + G_H$; $G_{(NO_2^-)calc.} = 2G_{OH}$, and

$$G_{(N_2O)calc.} = \tfrac{1}{2}(G_H + G_{OH})$$

Substituting the accepted values for G_H and G_{OH} at the various pH values than

At neutral pH

$$G_{(-NO)calc.} = 10.1,\ G_{(NO_2^-)calc.} = 4.8,\ G_{(N_2O)calc.} = 2.65.$$

At pH 2.20

$$G_{(-NO)calc.} = 11.4,\ G_{(NO_2^-)calc.} = 5.4,\ G_{(N_2O)calc.} = 3.0$$

and at pH 0.45

$$G_{(-NO)calc.} = 12.4,\ G_{(NO_2^-)calc.} = 5.8,\ G_{(N_2O)calc.} = 3.3$$

Reaction (6) is known to be very rapid[33] and is important in the radiation chemistry of nitrite ion in aqueous solution.[32] Reaction (7) has been postulated by Weiss[41] and other workers[58] and is undoubtedly energetically favourable being approximately 95 k. cals. mole.$^{-1}$ exothermic (see Tables 12 and 13). This sequence of reactions was however rejected on several grounds.

(a) The calculated yields on the basis of this scheme are not in such good agreement with experiment as the former mechanism.

(b) Assuming the intermediary is HONO, then using the thermochemical data in Tables 12 and 13, together with D(H —— NO) = 48 k. cals./mole., then reaction 5 is approximately 34 k. cals./mole. endothermic.

TABLE 13

Specie	Reference Number	k. cals. per mole.		
		Standard Heat of formation (gaseous)	Heat of solution	Heat of formation (aqueous)
H_2O	55	-57.8	-10.5	-68.3
HONO	55	-21 ± 0.2	-7.0*	-28.0
NO_2	56	8.1	-5.0*	+ 3.0

* assumed values.

(c) In a study of the gas phase reaction

$$H_2 + NO_2 = H_2O + NO$$

by Ashmore[59] et al., it was found that the reaction was inhibited by nitric oxide. The overall process was described

by a chain mechanism in which the action of nitric oxide was attributed to the reaction

$$No + OH + M = HNO_2 + M$$

where the third body M = H_2. However HNO_2 was not a stable product under these reaction conditions (approximately 450°C) and could not be detected.

In our experiments (M = water) it is difficult to envisage that reaction (1) yields any other product than nitrite. Consequently this alternative scheme did not appear to merit serious consideration and was therefore rejected.

The molecular product yields and their significance with respect to the reaction mechanism.

On the basis of the proposed mechanism it is found that in neutral solution the calculated yields for nitric oxide consumption and nitrite production are some 10% less than the observed experimental values. At the same time the molecular product yields of hydrogen peroxide and hydrogen, $G_{(H_2O_2)} = 0.52$, and $G_{(H_2)} = 0.40$, are less than the accepted primary yields for these products, i.e. $G_{H_2O_2} = 0.71$, and $G_{H_2} = 0.45$. It is suggested that these discrepancies are best attributed to the efficient scavenging of the precursors of molecular hydrogen peroxide and hydrogen by nitric oxide in the spur, the free radical yield thus being effectively increased at the expense of the molecular product yields.

The alternative explanations (a) that a thermal reaction occurs between nitric oxide and hydrogen peroxide to produce

nitrite, or (b) a competition exists between the molecular products and nitric oxide for the primary radicals, are regarded as unsatisfactory. Arguments to this effect are briefly presented below.

(a) It has been shown that in the gas phase at 300°C,[60] hydrogen peroxide reacts rapidly with nitric oxide, the overall reaction being represented by

$$H_2O_2 + NO = NO_2 + H_2O$$

A similar but slower reaction can be envisaged in solution, followed by

$$NO_2 + NO + H_2O = 2HNO_2$$

so that overall we have

$$H_2O_2 + 2NO = 2HNO_2$$

The calculated yields for $G_{(-NO)}$ and $G_{(NO_2^-)}$ would thus be increased giving the corrected values

$$G_{(-NO)} = 3G_H + G_{OH} + 2\left[G_{H_2O_2} - G_{(H_2O_2)}\right] = 11.5$$

and

$$G_{(NO_2^-)} = G_H + G_{OH} + 2\left[G_{H_2O_2} - G_{(H_2O_2)}\right] = 5.7$$

Although a thermal reaction with this approximate stoichiometry has been indicated previously (Table 9) its rate would appear to be far too slow for any detectable contribution of this nature to occur during an irradiation.

(b) If it is to be implied that the molecular hydrogen peroxide or hydrogen can effectively compete with 10^{-3}M concentrations of nitric oxide for the OH or H radicals, then one must assume that the rate constants for reactions (1) and (2), k_1 and k_2, are several orders of magnitude less than those of (8), (9) and (10).

$$OH + H_2O_2 = HO_2 + H_2O \quad \ldots\ldots\ldots (8)$$
$$OH + H_2 = H + H_2O \quad \ldots\ldots\ldots (9)$$
$$H + H_2O_2 = OH + H_2O \quad \ldots\ldots\ldots (10)$$

This assumption is clearly untenable for several reasons.

(i) Reactions (8) and (9) involve bond breakage and might be expected to be slower than (1) which is essentially a radical reaction, presumably requiring little or no activation energy. Furthermore it is known that OH radicals react rapidly with nitrite ion as in

$$OH + NO_2^- = NO_2 + OH^- \quad \ldots\ldots\ldots (11)$$

and that $k_{11}/k_8 = 55 \pm 20$[32] $= k_{11}/k_9$[61]. Consequently as the concentration of nitrite produced in these experiments exceeds that of the molecular products by a factor of about 10, any effective competing reaction would be expected to occur by (11) and not (8) or (9).

(ii) The failure to detect any consumption of hydrogen peroxide or difference in the product yields during the irradiation of solutions of nitric oxide containing 1 to 1.5 x 10^{-4}M H_2O_2, indicates that all the radicals are reacting with nitric oxide. The explanation of the post irradiation effect observed in such solutions must await further investigation.

<u>The effect of solute concentration on the molecular yields and its significance in the nitric oxide system.</u>

It is well known that the molecular yields decrease with increase in the concentration of solute present in solution. Sworski[62] made the first accurate study of this effect on the yield of hydrogen peroxide in aerated acid solution as a function of bromide concentration, and this was later

extended to neutral solution by Allen and Holroyd.[63] It was found empirically that the decrease in $G_{H_2O_2}$ was linear in the cube root of the bromide concentration. Subsequently Schwarz[64] observed a similar effect with respect to the hydrogen yields. In all cases it is found that solutes known or expected to react with OH radicals decrease $G_{H_2O_2}$, while those expected to react with H atoms reduce G_{H_2}. Solutes which can react with both radicals such as nitrite ion, reduce both $G_{H_2O_2}$ and G_{H_2}. It is likely that nitric oxide belongs to this latter category.

If one assumes that nitric oxide reacts as rapidly as nitrite ion with H and OH, (it is shown in chapter V that the first assumption is fully justified for the precursors of molecular hydrogen in neutral solution) then from the data of Schwarz,[64] and Schwarz and Salzman[65], one would expect at a concentration of 10^{-3}M that $G_{H_2} = 0.41$, and $G_{H_2O_2} = 0.61$. The results obtained with solutions of nitric oxide approximately comply with such assumptions. As the four quantities G_H, G_{OH}, G_{H_2} and $G_{H_2O_2}$ are connected by the equation of material balance

$$G_{-H_2O} = G_H + 2G_{H_2} = G_{OH} + 2G_{H_2O_2}$$

any decrease in the molecular product yields due to such scavenging is reflected in an apparent increase in the radical yields.

Substituting the appropriate values in the case of nitric oxide solutions at neutral pH we have

$$G_{H(\text{apparent})} = G_H + 2\left[G_{H_2} - G_{(H_2)}\right] = 3.0$$

and

$$G_{OH(\text{apparent})} = G_{OH} + 2\left[G_{H_2O_2} - G_{(H_2O_2)}\right] = 2.8$$

On this basis the calculated values for nitric oxide consumption and nitrite production will now be given by

$$G_{(-NO)calc.} = 3G_H + G_{OH} + 6\left[G_{H_2} - G_{(H_2)}\right] + 2\left[G_{H_2O_2} - G_{(H_2O_2)}\right] = 11.8$$

and

$$G_{(NO_2^-)calc.} = G_H + G_{OH} + 2\left[G_{H_2} - G_{(H_2)}\right] + 2\left[G_{H_2O_2} - G_{(H_2O_2)}\right] = 5.8$$

Similarly

$$G_{(N_2O)} = G_H + 2\left[G_{H_2} - G_{(H_2)}\right] = 3.0$$

The corrected expressions give values in very good agreement with experiment and the overall material balance for the consumption of nitric oxide is adequately represented by

$$4NO + H_2O = 2HNO_2 + N_2O$$

For convenience in later discussions the calculated values are taken to be equivalent to the experimental values and are represented by G°, with the corresponding formula in parentheses, as in $G^\circ_{(NO_2^-)}$.

Kinetic Studies

It has been shown (Figure 15) that as greater than about 50% of the nitric oxide is consumed, then the rate of the reaction decreases. This indicates that a back reaction involving one or both reaction products becomes of increasing importance as their ratio in the solution increases. It has already been indicated that nitrite ion reacts rapidly with both the OH radical and the reducing specie, while it is also known that nitrous oxide reacts only with the latter. This suggested a study of mixtures of nitric oxide in the presence of nitrite or nitrous oxide, from which it should

be possible

(1) to substantiate the above reaction mechanism,

(2) ascertain competition constants relative to these solutes and nitric oxide, and

(3) correlate such data with that well established for oxygen.

The results and discussion of such experiments are presented in the following chapter.

A study of the effect of bromide ion which reacts only with the OH radical was also investigated, and the results of these experiments are also presented and discussed in the next chapter.

CHAPTER V

THE RADIOLYSIS OF SOLUTIONS OF NITRIC OXIDE CONTAINING ADDED NITRITE ION; NITROUS OXIDE, AND BROMIDE ION

Chapter V

Introduction.

In neutral solution both nitrite and nitrous oxide are known to react rapidly with the reducing specie formed in water radiolysis, until recently commonly regarded as the hydrogen atom. A considerable amount of evidence, based mostly on pH studies, indicates however that two forms of a reducing entity, differing in constitution and reactivity, can coexist in aqueous solutions. Consequently a preliminary discussion of this aspect is presented below because of its relevance to the interpretation of the studies which follow.

(1) The nature of the reducing species in water radiolysis.

It has been postulated that the hydrogen atom may react either as H, a solvated electron[66] (e^-_{aq} or $H_2O^-_{aq}$) which can be equated with the negative polaron of Weiss[67] or as H_2^+. These three species can be regarded as neutral, basic and acidic forms respectively. There is considerable evidence that the latter specie exists in strong acid solution and this constitution was originally invoked to explain the oxidation of ferrous sulphate[68] and later iodide ion[69] in solutions of sulphuric acid. The results of Halpern et al.[70] and Czapski et al.[71] now indicate that H_2^+ does not play a prominent role in the former case.

Barr and Allen[72] were the first to indicate that two forms of hydrogen atom could exist in neutral solution. They were able to show that the product of the reaction OH + H_2, written in their paper as

$$OH + H_2 = H_2O + H'$$

reacted preferentially with oxygen rather than with hydrogen peroxide, whereas radicals produced in water radiolysis react about equally rapidly with both. The possibility that the radical formed in water radiolysis was either a solvated electron or a hydrogen atom, while the reaction of $OH + H_2$ in aqueous solution give rise to H_2^+, instead of H, was considered but could not be distinguished. However independent studies by Dainton et al.[73] and more recently Czapski et al.[74] and Hochanadel,[10] indicate that the $OH + H_2$ reaction produces a true H atom. Studies with respect to the influence of pH on hydrogen yields in air free solutions of methanol,[66] isopropanol,[75] and chloracetic acid[76] were also consistent with the presence of two species. The overall evidence suggested that a reaction of the form

$$H_3O^+ + H_2O^- = H + H_2O$$

expressed the relation between the two species, the hydrogen ion competing with the organic solutes (RH_2) for the solvated electron to give a more acid form H, which then reacted as in

$$RH_2 + H = RH + H_2$$

to form hydrogen. The results obtained in a number of inorganic systems[77-83] were also explicable in terms of the above relation between the two species, and it has been recently demonstrated in studies based on the kinetic salt effect by Czapski and Schwarz,[84] and Collinson et al.,[85] that the reducing entity present at neutral pH has a unit negative charge and may therefore be considered as the solvated electron. Furthermore the identification of the form present

in acid solution with the true hydrogen atom has also been demonstrated,[10,74,86] and in addition Jortner and Rabani[86] provide evidence in favour of the reaction

$$H + OH^- = e^-_{aq}$$

at about pH 11.

A conflict regarding the composition of the total yield of reducing specie present at neutral pH does however exist between the results obtained in the radiolysis of organic compounds[75,76] and those in the oxygen - hydrogen peroxide system as studied by Ozapski and Allen.[83] The former workers indicate that both forms exist in neutral solution, a yield of $G_H = 0.6$ being attributed to the H atom and the balance by the solvated electron, $G_{H_2O^-} = 2.3$ Striking evidence in support of this has been provided by Rabani[87] who irradiated a series of organic compounds, including methanol and isopropanol, in the presence of an electron scavenger such as bicarbonate ion. In each case it was found that $G_{(H_2)}$ attained a low limiting value of 1.05 ± 0.04, which on adopting a value of 0.5 for the molecular yield G_{H_2} indicates an independent yield of $G_H = 0.55$. In addition a kinetic study showed these H atoms to be equivalent to true hydrogen atoms. In contrast the results obtained in the presence of oxygen[83] indicate that the whole of the reducing specie exists as solvated electrons, i.e. $G_{H_2O^-} = 2.85 \pm 0.15$. Hayon[88] suggests that the independent yield of H in organic solutions results from the decomposition of excited water molecules[75] (H_2O^*)

$$H_2O^* = H + OH$$

and is not observed in the presence of oxygen due to the

quenching of H_2O^* as in

$$H_2O^* + O_2 = H_2O^+ + O_2^-.$$

However this controversy has yet to be completely resolved.

Dainton[77-79] in a study of the radiation chemistry of solutions containing nitrous oxide has postulated the existence of a further latent specie which becomes manifest only in the presence of strong acid or alkali.[89] This intermediate is assumed to be either an excited water molecule or an isolated radical pair in a solvent cage, denoted by (H + OH). Its reaction with acid is represented by the equations

$$H_2O^* + H^+_{aq} = H_2^+{}_{aq} + OH_{aq}$$

$$(H + OH) + H^+_{aq} = H_2^+{}_{aq} + OH_{aq}$$

and with alkali by

$$H_2O^* + OH^-_{aq} = e^-_{aq} + OH_{aq}$$

$$(H + OH) + OH^-_{aq} = e^-_{aq} + OH_{aq}$$

Such a hypothesis accounts for the recently established increase in free radical yields with increase in pH[89] in the region 11 to 14, together with the well known increase in radical yields with the decrease in pH from 3 to zero. The conventional hydrogen atom yield in strong acid solution was thus represented as the sum of $G_{H_2O^-}$, G_H and $G_{H_2^+}$. An alternative explanation of this pH effect similar to the above view is discussed by Hart and Platzman.[5] These authors suggest that in strong sulphuric acid solutions, water sub excitation electrons[90] may excite bisulphate ions which then subsequently decompose to yield two extra radicals

$$HSO_4^- . H_2O + e^-_{s.e.} = HSO_4 + H + OH^- + e^-$$

Similar excitation and decomposition of the hydroxyl radical was postulated in solutions of about pH 12, and this coincides with the onset of increased radical yield detected by Dainton and Watt[89] in alkaline solution.

In conclusion one can briefly summarise that throughout the acid pH range the evidence is consistent with the relationships

$$H_2O^- \text{ or } e^-_{aq} \xrightarrow{H^+ (\text{or } H_3O^+)} H \xrightarrow{H^+} H_2^+$$

H_2^+ becoming kinetically important at low pH values only in systems where no other acceptor can directly and rapidly react with H_2O^- or H by alternative mechanisms.[74]

(2) The irradiation of solutions of nitric oxide at their natural pH in the presence of sodium nitrite.

(a) Results:

In these experiments A.R. sodium nitrite was used without further purification. A series of solutions were prepared at their natural pH with various nitric oxide and nitrite concentrations and different nitric oxide to nitrite ratios. Samples were irradiated so that not greater than about 40% of the nitric oxide was consumed and the solutions subsequently analysed to determine the residual nitric oxide and the increased concentration of nitrite. Such analyses were subject to greater experimental errors with the higher nitric oxide to nitrite ratios. These arose largely as a result of the small uncertainty always associated with the estimation of the 5 ml. volumes of solution delivered by the syringe. Any small error here was considerably magnified in the ultimate determination of the nett production of nitrite and the corresponding consumption of nitric oxide. The

consumption of nitric oxide and the production of nitrite were observed to be linear with dose, but the rates of consumption and production, respectively, decreased with increasing nitrite to nitric oxide ratios. Figure 21 shows the dose - concentration curves obtained with two different mixtures in comparison with those obtained in the absence of added nitrite ion (dotted lines). The values obtained for the respective yields, which represent the mean of at least three separate irradiation experiments per mixture, are summarised in Table 14, together with the average $(NO)/(NO_2^-)$ ratio present during an irradiation.

The variation in pH in these experiments is much less significant than in solutions containing nitric oxide alone, the sodium nitrite effectively suppressing the dissociation of the nitrous acid produced during irradiation. The pH of a solution approximately 3×10^{-4}M in HNO_2 and 6×10^{-4}M in $NaNO_2$ was found to be 4.2. This mixture approximately represents the lowest final ratio of $NaNO_2$ to HNO_2 observed in this work and indicates that the pH throughout these experiments was always greater than 4.0.

(b) Discussion

The radiation chemistry of nitrite ion at neutral pH has been studied by Schwarz and Allen[32] and extended by Schwarz and Salzman.[65] The reducing entity then designated by H is now best represented by the solvated electron H_2O^-, and the kinetics of the reaction are consistent with the following mechanism:-

Figure 21

Nitric Oxide Consumption and Nitrite Production in solutions containing added Nitrite ion.

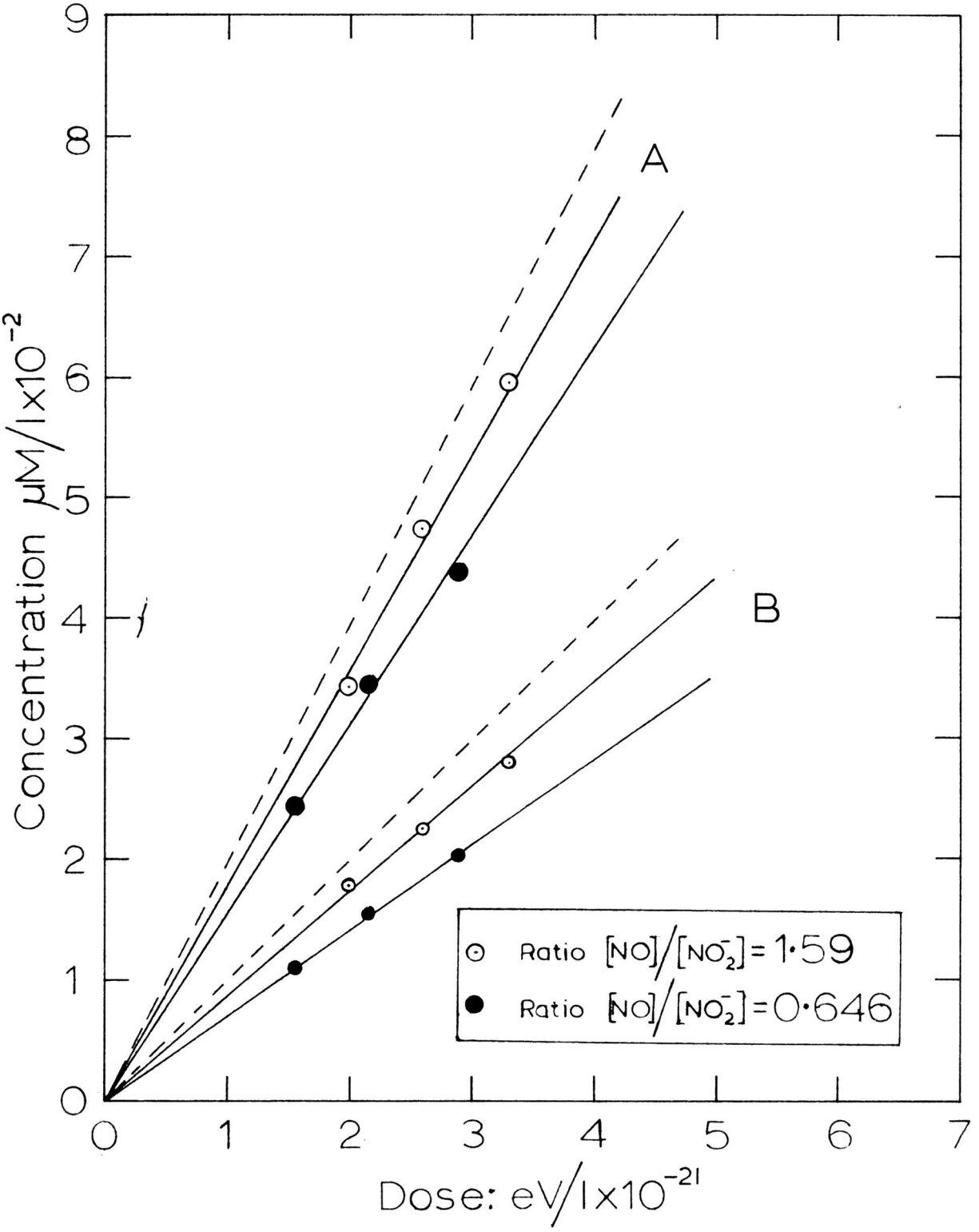


TABLE 14

Initial Nitric Oxide concentration x 10^3M.	Initial Nitrite concentration x 10^3M.	Average $(NO)/(NO_2^-)$	Mean $G^x_{(-NO)}$	Mean $G^x_{(NO_2^-)}$
1.785	1.925	0.671	10.72	4.00
1.64	3.88	0.326	8.38	3.52
1.793	0.897	1.32	11.78	5.14
1.91	0.58	2.20	11.75	5.40
1.285	0.542	1.59	10.76	5.24
0.797	0.808	0.702	10.02	4.46
1.083	1.237	0.646	9.43	4.27
0.94	2.00	0.353	8.26	4.15
1.11	1.99	0.409	8.65	3.46
1.57	1.00	1.12	9.92	4.88
1.519	1.457	0.932	10.9	4.88

$$H_2O = H_2, H_2O_2, OH, H_2O^-$$

$$OH + NO_2^- = NO_2 + OH^- \quad \text{.....(i)}$$

$$H_2O^- + NO_2^- = NO + 2OH^- \quad \text{.....(ii)}$$

$$H_2O^- + H_2O_2 = H_2O + OH + OH^- \quad \text{.....(iii)}$$

$$NO_2 + NO + H_2O = 2HNO_2 \quad \text{.....(iv)}$$

$$2NO_2 + H_2O = HNO_2 + HNO_3 \quad \text{.....(v)}$$

When a nitrite solution is irradiated all the NO formed in (ii) reacts with the NO_2 formed in (i) and no nett decomposition is observed (iv). When H_2O_2 is present in a concentration comparable to that of nitrite, an effective competition for H_2O^- can occur (iii) and consequently nitrite is oxidised faster by OH than it is reduced by H_2O^-. The excess NO_2 so formed then hydrolyses to yield nitrate as shown in the last equation (v).

Czapski and Schwarz[84] have recently represented equation (ii) by an electron transfer process

$$H_2O^- + NO_2^- = NO_2^= + H_2O \quad \text{.....(vi)}$$

and equation (iv) by

$$NO_2 + NO_2^= = 2NO_2^- \quad \text{.....(vii)}$$

Such formulations are stoichiometrically indistinguishable from (ii) and (iv) and do not therefore affect the above conclusions.

On the basis of the postulated mechanism for the radiolysis of nitric oxide and the above reaction scheme for nitrite, the following series of radical reactions can occur in solutions containing both these solutes.

$$H_2O = H_2, H_2O_2, OH, H_2O^-$$

$$H_2O^- + NO = HNO + OH^- \quad \text{.....(1)}$$

$$HNO + NO = N_2O + OH \quad \text{.....(3)}$$

$$H_2O^- + NO_2^- = NO + 2OH^- \quad \ldots\ldots\ldots (4)$$

$$OH + NO = HNO_2 \quad \ldots\ldots\ldots\ldots (5)$$

$$OH + NO_2^- = NO_2 + OH^- \quad \ldots\ldots\ldots (6)$$

$$NO_2 + NO + H_2O = 2HNO_2 \quad \ldots\ldots\ldots\ldots (7)$$

A kinetic treatment of this reaction scheme (Appendix II) shows that

$$G^x_{(-NO)} = G^\circ_{(-NO)} - 4\alpha G_{H_2O^-} \quad \ldots\ldots\ldots\ldots (A)$$

$$G^x_{(NO_2^-)} = G^\circ_{(NO_2^-)} - 2\alpha G_{H_2O^-} \quad \ldots\ldots\ldots\ldots (B)$$

$$G^x_{(N_2O)} = G^\circ_{(N_2O)} - \alpha G_{H_2O^-} \quad \ldots\ldots\ldots\ldots (C)$$

where G^x = product yield in the presence of added nitrite ion, at concentration x, and G° = the experimentally derived yield in the absence of added nitrite ion.

Rearranging these equations we have

$$\left[G^\circ_{(-NO)} - G^x_{(-NO)}\right]^{-1} = \frac{1}{4G_{H_2O^-}}\left[1 + k_1(NO)/k_4(NO_2^-)\right] \ldots(D)$$

$$\left[G^\circ_{(NO_2^-)} - G^x_{(NO_2^-)}\right]^{-1} = \frac{1}{2G_{H_2O^-}}\left[1 + k_1(NO)/k_4(NO_2^-)\right] \ldots(E)$$

$$\left[G^\circ_{(N_2O)} - G^x_{(N_2O)}\right]^{-1} = \frac{1}{G_{H_2O^-}}\left[1 + k_1(NO)/k_4(NO_2^-)\right] \ldots(F)$$

where $\alpha = \left[1 + k_1(NO)/k_4(NO_2^-)\right]^{-1}$.

From these equations it can be seen that the reciprocal should be a linear function of the nitric oxide to nitrite ratio. Using the values for $G^x_{(-NO)}$ and $G^x_{(NO_2^-)}$ presented in Table 14 together with $G^\circ_{(-NO)} = 12.0$, and $G^\circ_{(NO_2^-)} = 5.9$, the reciprocals of equations D and E were plotted as a function of the average $(NO)/(NO_2^-)$ concentrations present during an irradiation (Figures 22 and 23). In both cases $G_{H_2O^-}$ was taken as 2.9 so that the intercepts represent $1/4\ G_{H_2O^-}$ and

Figure 22

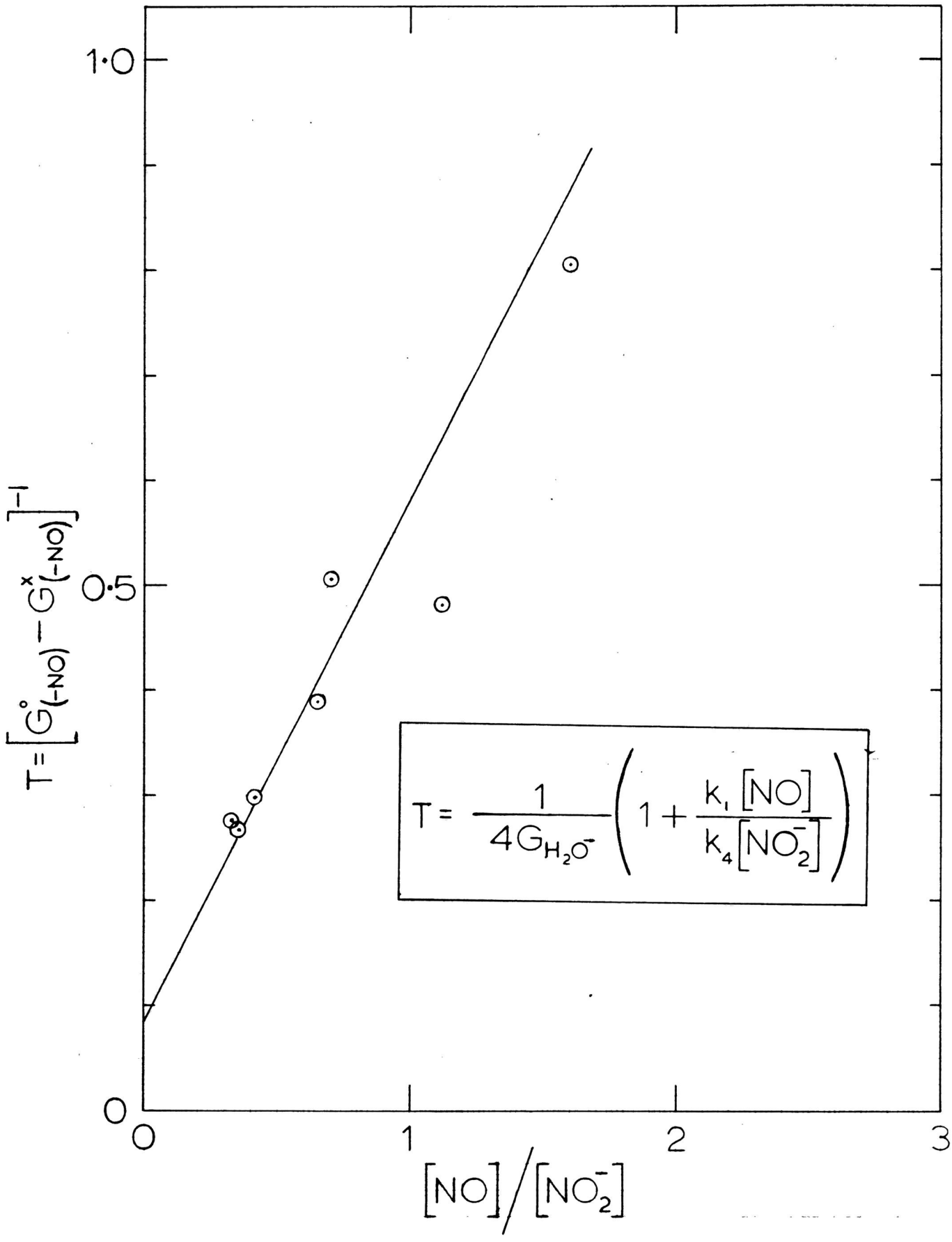
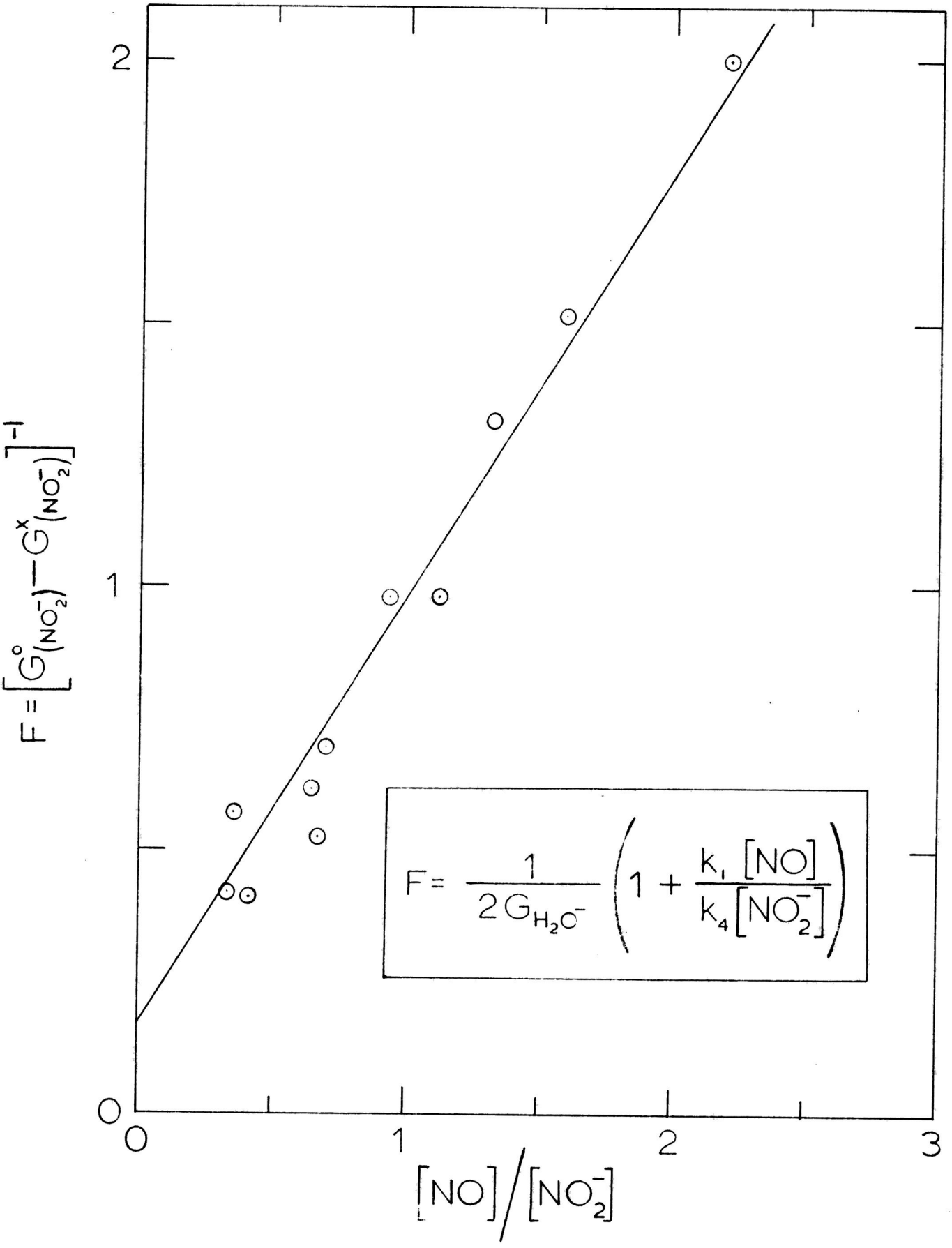

1·0
0·5
0
0
1
2
3
$T=\left[G^{\circ}_{(-NO)}-G^{x}_{(-NO)}\right]^{-1}$
$[NO]/[NO_2^-]$
$T=\frac{1}{4G_{H_2O^-}}\left(1+\frac{k_1[NO]}{k_4[NO_2^-]}\right)$

Figure 23


2
1
0
0
1
2
3
$F = \left[G^{\circ}_{(NO_2^-)} - G^{x}_{(NO_2^-)}\right]^{-1}$
$[NO]/[NO_2^-]$
$F = \frac{1}{2G_{H_2C^-}}\left(1 + \frac{k_1[NO]}{k_4[NO_2^-]}\right)$

$1/2G_{N_2O^-}$, respectively. It can be seen that the experimental results are in good agreement with these relations and therefore substantiate the proposed mechanism for the radiolysis of nitric oxide solutions. The value of the competition constant $k_1(H_2O^- + NO)/k_4(H_2O^- + NO_2^-)$, deduced from the slopes of Figures 22 and 23 was found to be 5.7 and 4.7, respectively. Since the analytical determinations for nitrite were subject to the least experimental error, the latter value was adopted (N.B. in Figure 22 only the more consistent values of $G^x_{(-NO)}$ are plotted).

When nitric oxide solutions are irradiated alone, such a competition must become of increasing importance as the concentration of nitrite builds up in the solution. If the nitrite ion is the only effective competing solute in this system, then it should be possible to reproduce the entire course of the reaction, for each product, by the use of the equations A, B and C. To enable the simple integration of these equations it was assumed that the ratio of nitric oxide to nitrite in the irradiated solution would be approximately expressed by the relation

$$y = P - qx$$

where

P = initial concentration of NO

y = concentration of NO at any instant

x = concentration of NO_2^- at any instant

and $q = G_{(-NO)}/G_{(NO_2^-)} = 12.0/5.9 = 2.034.$

Similarly it was assumed that the concentration of nitrous oxide in the irradiated solutions in terms of y and x could

be expressed in the form

$$y = P - fqz$$

where

z = concentration of N_2O at any instant,

and $f = G_{(NO_2^-)} / G_{(N_2O)} = 5.9/3.1 \cong 2.0$

Taking as the unit of dose, t, the input of 100 eV/l and as the unit of concentration, molecules/l, then equations A, B and C take the form

$$-\frac{dy}{dt} = G^{\circ}_{(-NO)} - \frac{4G_{H_2O^-}}{1 + 4.7y/(P-y)q} \quad \ldots\ldots\ldots\ldots \text{(G)}$$

$$\frac{dx}{dt} = G^{\circ}_{(NO_2^-)} - \frac{2G_{H_2O^-}}{1 + 4.7(P-qx)/x} \quad \ldots\ldots\ldots\ldots \text{(H)}$$

and

$$\frac{dz}{dt} = G^{\circ}_{(N_2O)} - \frac{G_{H_2O^-}}{1 + 4.7(P-fqz)/fz} \quad \ldots\ldots\ldots\ldots \text{(I)}$$

On integration taking $G_{H_2O^-} = 2.9$, $G^{\circ}_{(-NO)} = 12.0$, $G^{\circ}_{(NO_2^-)} = 5.95$ and $G^{\circ}_{(N_2O)} = 3.1$, then equations (G), (H) and (I) assume a logarithmic form as in equations (J), (K) and (L), respectively.

$$t/p = 7.48 \times 10^{-2} - 7.48 \times 10^{-2} y/p - 8.47 \times 10^{-3} \ln\left(\frac{114.4y + 0.4P}{114.4P + 0.4P}\right) \quad \ldots \text{(J)}$$

$$t/p = 0.15x/p - 8.41 \times 10^{-3} \ln(-2.03x/p + 1) \quad \ldots\ldots\ldots \text{(K)}$$

and

$$t/p = 0.29z/p - 7.88 \times 10^{-3} \ln(-4.04z/p + 1) \quad \ldots\ldots\ldots\ldots \text{(L)}$$

(see appendix III for a more complete derivation of these equations).

Using a value of P = 1.93×10^{-3}M then the theoretical curves (dotted lines in Figure 24) derived from these equations for various concentrations of x, y and z (Table 15) are found to agree well with the experimental results obtained previously (see Figures 14 and 15). The overall radiolysis of nitric oxide at neutral pH can therefore be adequately explained in terms of a competition for the solvated electron between the residual concentration of nitric oxide and the radiation induced nitrite ion.

The equations A, B and C can also be used to determine the deviation of the respective product concentrations from what they would be if the initial yields were maintained throughout the irradiation. Considering only equation B (since the determinations of nitrite concentration were subject to the least experimental error) then on integration, expansion, and neglect of higher order terms (see Appendix IV) we have

$$G^{\circ}_{(NO_2^-)}t = x + \frac{x^2 G_{H_2O^-}}{G^{\circ}_{(NO_2^-)} \cdot k_1 P/k_4}$$

which on substitution $G^{\circ}_{(NO_2^-)} = 5.9$, $k_1/k_4 = 4.7$ and $G_{H_2O^-} = 2.9$, becomes

$$G^{\circ}_{(NO_2^-)}t = x + \frac{0.104x^2}{P}$$

Here the correction term in x^2 gives the concentration of nitrite ion at any given dose t, to be added to that of x, the measured concentration of nitrite. In the case of a solution of nitric oxide initially 1.93×10^{-3}M, and sub-

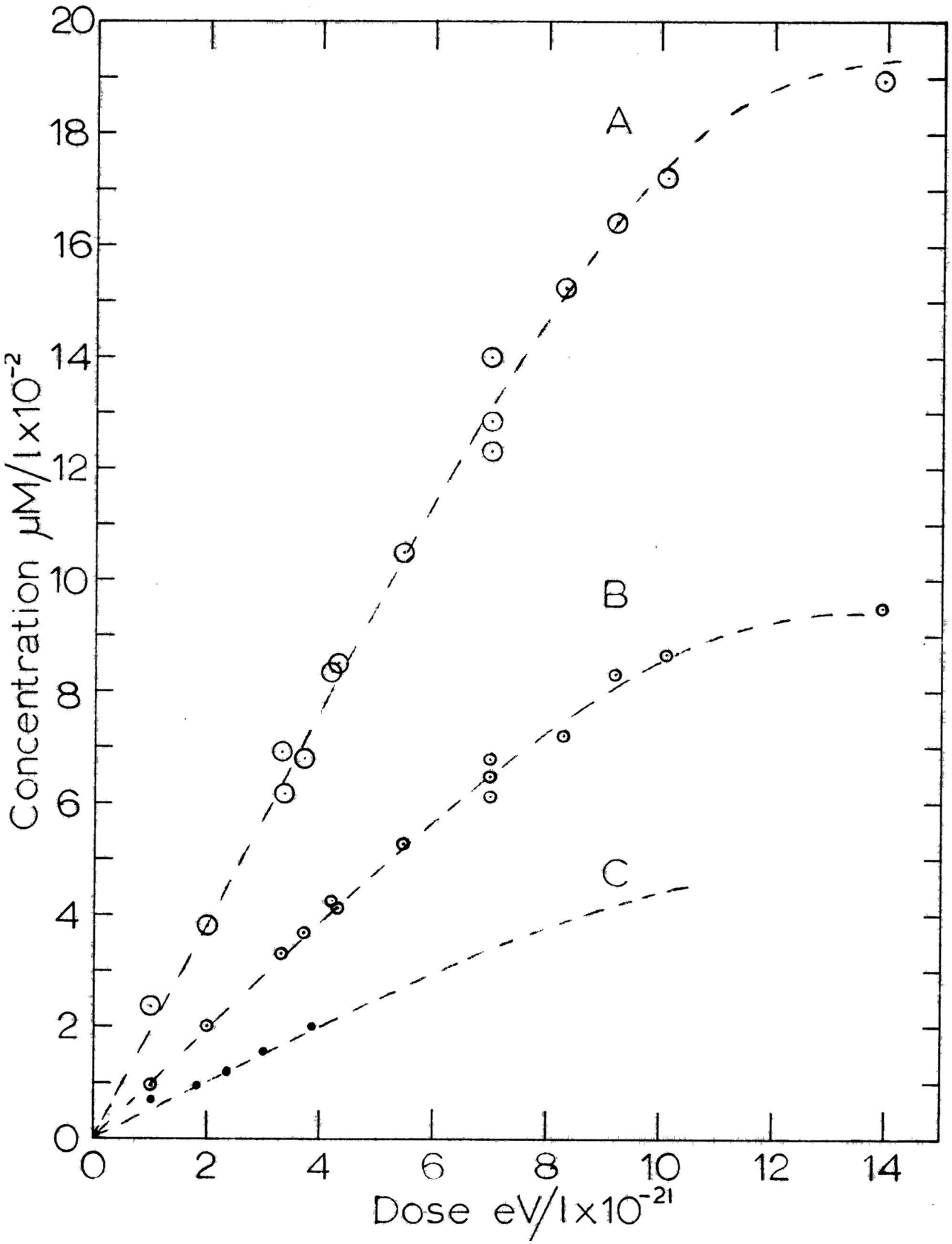
TABLE 15

Calculated Dose (ev/1 x 10^{21})	Concentration of x (x 10^{-4}M)	Calculated Dose (eV/1 x 10^{21})	Concentration of y (x 10^{-4}M)	Calculated Dose (ev/1 x 10^{21})	Concentration of z (x 10^{-4}M)
1.018	1.0	1.01	17.3	1.97	1.0
2.05	2.0	1.72	16.0	4.0	2.0
4.17	4.0	4.84	10.0	6.16	3.0
6.43	6.0	5.96	8.0	8.67	4.0
9.08	8.0	8.43	4.0	10.47	4.5
11.07	9.0	10.02	2.0		
13.03	9.4	11.11	1.0		
		13.34	0.1		

Figure 24

The dotted lines designated by A, B and D, represent the consumption of nitric oxide, and the production of nitrite and nitrous oxide, as calculated by equations J, K and L, respectively. The experimental points for nitrous oxide are those previously presented in Figure 14, while those for nitric oxide and nitrite were previously presented in Figure 15.

Figure 24


Concentration μM/l x10⁻²
Dose eV/l x10⁻²¹
A
B
C
0
2
4
6
8
10
12
14
16
18
20

sequently irradiated to 50% complete consumption, the correction term approximately amounts to 2½% of the measured concentration; i.e. x approximately equals 4.75×10^{-4}M, while the x^2 term amounts to about 0.12×10^{-4}M. As this x^2 correction factor is within experimental error and decreases relative to that of x with lower values of t, corrections of this nature were of little significance and the initial yield values previously determined were not modified by additional corrections of this order.

(3) Correlation of the above data with that well established for solutions containing oxygen.

(a) The relation of $k_{(H_2O^- + NO)}$ to $k_{(H_2O^- + O_2)}$

Schwarz and Allen[32] have shown that

$$k_{(H_2O^- + NO_2^-)} / k_{(H_2O^- + H_2O_2)} = 0.47$$

while Schwarz and Salzman[65] indicate that this same constant is more nearly 0.30.

Combining these values with that of Czapski and Allen[83] for

$$k_{(H_2O^- + O_2)} / k_{(H_2O^- + H_2O_2)} = 2.0$$

then values of

$$k_{(H_2O^- + O_2)} / k_{(H_2O^- + NO_2^-)}$$ range from 4.26 to 6.66.

It can be seen that the value obtained for

$$k_{(H_2O^- + NO)} / k_{(H_2O^- + NO_2^-)} = 4.7$$

is of the same order of magnitude as the corresponding constants for oxygen and this indicates that

$k_{(H_2O^- + NO)}$ approximately equals $K_{(H_2O^- + O_2)}$.

(b) It should be possible to obtain a much more precise value for the constant $k_{(H_2O^- + NO)} / k_{(H_2O^- + NO_2^-)}$ by

a determination of $G^{x}_{(N_2O)}$ as a function of the $(NO)/(NO_2^-)$ ratio, plotted according to equation (F). In this case the accurate analytical determination of the nitrous oxide concentration would not be rendered more difficult in the presence of large nitrite concentrations, a feature inevitable in the former determinations of $G^{x}_{(-NO)}$ and $G^{x}_{(NO_2^-)}$. At the same time the slope of such a curve could be used to infer with reasonable accuracy the value of the intercept and hence the total yield of reducing specie reacting with nitrite and nitric oxide at neutral pH.

In view of the controversy now existing with regard to the composition of the total yield of reducing specie present at neutral pH, such an experiment would afford a valuable comparison with the conclusions recently deduced by Czapski and Allen[83] for solutions containing dissolved oxygen. These workers have carried out an accurate study on the radiolysis of oxygen and hydrogen peroxide in solutions containing 10^{-4}M bromide ion. In neutral solution the reaction mechanism was written as

$$H_2O = H_2, H_2O_2, OH, H$$

$$OH + Br^- = Br + OH^- \quad \ldots\ldots\ldots\ldots\ldots \text{(I)}$$

$$Br + H_2O_2 = HO_2 + H^+ + Br^- \quad \ldots\ldots\ldots \text{(II)}$$

$$H + H_2O_2 = OH + H_2O \quad \ldots\ldots\ldots\ldots\ldots \text{(III)}$$

$$H + O_2 = HO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(IV)}$$

$$2HO_2 = H_2O_2 + O_2 \quad \ldots\ldots\ldots\ldots\ldots \text{(V)}$$

This mechanism predicts that in solutions containing both oxygen and hydrogen peroxide that

$$\left[G^{\circ} - G_{(H_2O_2)}\right]^{-1} = \frac{1}{2G_H}\left[1 + k_{IV}(O_2) / k_{III}(H_2O_2)\right]$$

where G° = initial peroxide yield in solutions containing oxygen but no peroxide,

and $G_{(H_2O_2)}$ = experimentally observed peroxide yield in the presence of added hydrogen peroxide.

This expression was accurately borne out by experiment, the measurements being sufficiently precise to indicate that $G_H = 2.85 \pm 0.15$. This value equals the accepted total yield of reducing radicals at neutral pH and was attributed to the solvated electron. No evidence was therefore provided for an independent yield of true H atoms, in contrast to the conclusions derived with neutral solutions of organic compounds in the absence of oxygen.

A few experiments were undertaken to determine the yield of N_2O in the nitric oxide - nitrite system, but due to lack of time and experimental difficulties had to be postponed. A single value of $G^{x}_{(N_2O)} = 2.4_1$ obtained with a $(NO)/(NO_2^-)$ ratio = 0.932, represented the most reliable data on this aspect. Substituting the values $G^{\circ}_{(N_2O)} = 2.9$, $G_{H_2O^-} = 2.9$ and $k_1/k_4 = 4.7$ in equation (C), together with the above ratio, then the predicted value $G^{x}_{(N_2O)} = 2.36$ is in accord with an initial yield $G_{H_2O^-} = 2.9$. However until more comprehensive data is available no significant conclusions can be drawn about the composition of the yield of reducing specie in the presence of nitric oxide.

(4) <u>The possible use of the nitric oxide - nitrite system at low pH</u>.

In neutral solution the results were expressed in terms of a competition for the solvated electron. By a similar

study in acid solution it may be possible to observe the corresponding competition for the H atom. Such a study is however complicated by two additional factors:-

(a) Unless nitric oxide is present, nitrite ion rapidly decomposes in acid solution to form nitrate (see chapter IV, section 3). Therefore to prepare solutions of low pH containing only nitric oxide and nitrite, a three stage process would need to be adopted.

(i) Preparation of neutral deaerated solutions of nitrite,

(ii) Preparation of the nitric oxide solution at the desired pH, and

(iii) Mixing of (a) to (b) with the aid of coupled syringes.

(b) Since the dissociation constant of nitrous acid equals 4.6×10^{-4} at 25°C, this acid would be undissociated in solutions of low pH. Consequently any competition observed for the reducing entity would presumably occur between HONO and NO and not NO_2^- and NO.

On this basis one can speculate that in acid solution, the following sequence of reactions would occur,

$$H_2O = H_2, H_2O_2, H, OH$$

$$H + NO = HNO \quad \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

$$HNO + NO = N_2O + OH \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

$$H + HONO = NO + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

$$OH + NO = HNO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$$OH + HONO = NO_2 + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

$$NO_2 + NO + H_2O = 2HNO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

From a consideration of the thermochemical data presented in Table 16, it can be seen that reactions (9) and (10) are certainly energetically favourable, being 84 and 39 k.cals. mole.$^{-1}$ exothermic, respectively. The corresponding reactions for nitrite ion, shown for comparison

$$H + NO_2^- = NO + OH^- \quad \ldots\ldots\ldots\ldots\ldots (11)$$

$$OH + NO_2^- = NO_2 + OH^- \quad \ldots\ldots\ldots\ldots\ldots (6)$$

are 63.5 and 28.5 k. cals. mole.$^{-1}$ exothermic, respectively. The above mechanism predicts that for the N_2O yield

$$G^a_{(N_2O)} = G^o_{(N_2O)} - \frac{G_H}{1 + k_{8(NO)}/k_{9(HONO)}}$$

where $G^a_{(N_2O)}$ = experimentally determined yield of N_2O in the presence of added nitrite of concentration a,

$G^o_{(N_2O)}$ = experimentally determined yield of N_2O in the absence of added nitrite, and

G_H = accepted yield of reducing specie at the appropriate pH.

If therefore the above assumptions are correct then it will be possible to obtain the value k_8/k_9.

Since reaction (9) involves a bond breaking process, while (8) is essentially a radical - radical reaction requiring no activation energy[53,54] and presumably occurring on every encounter, it would be expected that $k_8/k_9 \gg 1$. If this is so then an interesting comparison can be made with the reactions

$$H + O_2 = HO_2 \quad \ldots\ldots\ldots\ldots\ldots (12)$$

$$H + H_2O_2 = OH + H_2O \quad \ldots\ldots\ldots\ldots\ldots (13)$$

TABLE 16

Species	Reference Number	k. cals. mole^{-1}		
		Heat of formation gaseous	Heat of solution	Heat of formation aqueous
H	55	52.1	-1 ± 0.5	51.1 ± 0.5
OH	55	8.88 ± 0.5	-7 ± 2.5	2 ± 3
H_2O	55	-57.8	-10.5	-68.3
HONO	55	-21 ± 2	- 7 *	-28
NO_2	56	8.1	- 5.1 *	3
NO	56	21.6	- 4.6 *	17
NO_2^-	56			-25.4
OH^-	56			-54.96

* Assumed values.

for which Hochanadel[10] has shown that $k_{12}/k_{13} = 4.55 \times 10^3$, in good agreement with the independent estimate of 3×10^3 by Czapski and Allen.[83] It is also known that the weakest bonds in nitrous acid and hydrogen peroxide are the HO — NO and HO —OH bonds, for which the dissociation energies are 51 ± 2 and 50.3 ± 0.7 k. cals. mole.$^{-1}$ respectively.[55] Assuming that the frequency factors for reactions (12) and (13) are equal and the energy of activation for the former reaction (E_{12}), equal to zero then

$$k_{12}/k_{13} = 4.55 \times 10^3 = e^{(E_{13}-E_{12})/RT}$$

where R and T have their usual meaning. Solving this equation shows that E_{13} approximately equals 5 k. cal. mole.$^{-1}$ or about 10% of the HO - OH bond strength. If the energy of activation for reaction (9), E_9, is of this order of magnitude then k_8/k_9 will be approximately equivalent to k_{12}/k_{13} on taking E_8 as equal to zero. However any equality of k_8/k_9 with k_{12}/k_{13} would not indicate that $k_8/k_{12} = 1$, since the reactions of H atoms in (9) and (13) occur with two different solutes. A comparison of this nature may be achieved by a study in acid solution of the competition for H between nitric oxide and hydrogen peroxide.

Available data on the gas phase reactions of oxygen and nitric oxide with hydrogen atoms shows that the former reaction is some 10 to 20 times more rapid than the latter. Hoare and Walsh[91] deduce values for the third order rate constant of the reaction

$$H + O_2 + M = HO_2 + M$$

where M = H_2, of between 1.8 and 2.9×10^{17} cm.^{6}mole.$^{-2}$sec.$^{-1}$

at 20°C, while Clyne and Thrush[54] show that the corresponding constant for the reaction

$$H + NO + M = HNO + M$$

has a value of $(1.48 \pm 0.15) \times 10^{16}$ cm.^{6}mole.$^{-2}$sec.$^{-1}$, a little higher than their previous value[53] of 4.8×10^{15} cm.^{6}mole.$^{-2}$sec.$^{-1}$ In addition both these reactions are found to have negative activation energies with values of about 4 and 0.6 k.cals/mole., respectively, and it is also known that $k_{(H+O_2+M)}$ is some 6 times greater when M is H_2O than when M is H_2.[52] If these activation energies are applicable in solution then assuming $E_9 = E_{13}$, $k_8/k_9 \cong 14$, and will therefore be considerably less than k_{12}/k_{13}.

Finally it should be noted that k_8/k_9 cannot be equated with k_8/k_{11}. An unequivocal value for this latter ratio must be obtained in neutral solution and might be established by a study of the nitric oxide - nitrite competition for atomic hydrogen. A knowledge of this ratio would be important to interpret fully the nitric oxide - nitrite competition studies which were discussed earlier if evidence for an independent yield of H were to be obtained in this system.

(5) The irradiation of solutions of nitric oxide in the presence of nitrous oxide

Results:

(a) Pure water at natural pH

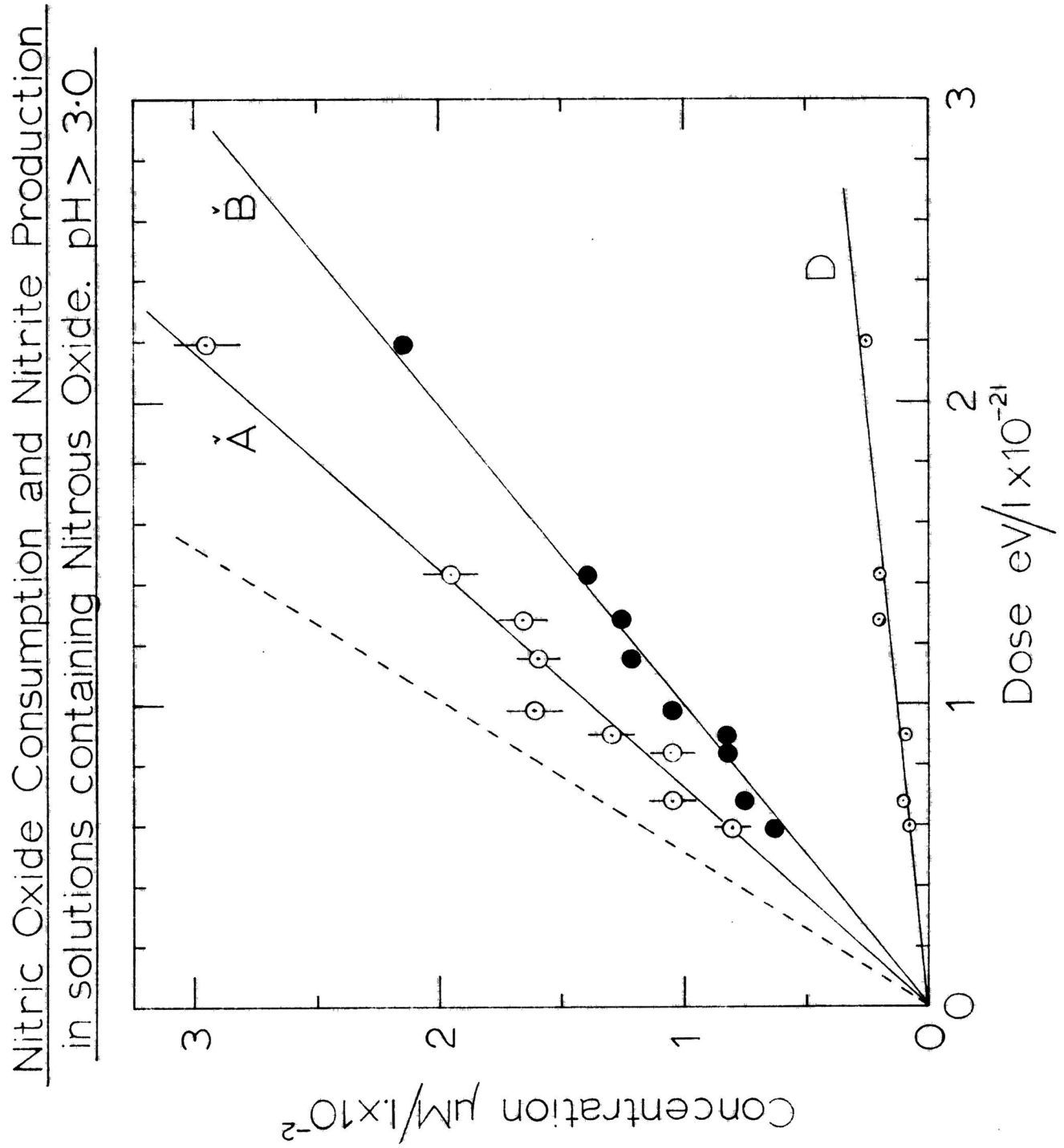
The nitrous oxide used in these experiments was supplied by the British Oxygen Co. Ltd. and the preparation of mixtures of nitrous and nitric oxides carried out in two stages.

(i) Saturated solutions of nitrous oxide were first obtained by substituting this gas for nitrogen prior to the generation of nitric oxide as described in chapter II, 4.

(ii) Nitric oxide was then bubbled through such a solution for about 3 to 5 minutes so that concentrations ranging from 3.5 to 7.0 x 10^{-4}M were obtained. It was assumed that the concentration of nitrous oxide remaining in the mixture would be approximately 10^{-2}M, the maximum solubility for this gas at 20°C being about 2.8 x 10^{-2}M. The nitrite blank observed in these solutions was approximately 10 to 15 x 10^{-6}M, indicating the presence of trace amounts of oxygen in the nitrous oxide.

Samples were irradiated so that no greater than 30 to 40% of the nitric oxide was consumed and the solutions subsequently analysed to determine the residual nitric oxide along with the production of nitrite and hydrogen peroxide. Since only small changes in concentration were being detected these analyses were subject to greater experimental error, mainly arising from the initial"syringe-volume" errors. The consumption of nitric oxide and production of nitrite were found to be linear with dose, and are shown in Figure 25

Figure 25


Nitric Oxide Consumption and Nitrite Production
in solutions containing Nitrous Oxide. pH > 3·0
Concentration μM/l.x10⁻²
Dose eV/l x10⁻²¹
A
B
D
0
1
2
3

along with the corresponding production of hydrogen peroxide. (The dotted line represents the consumption of nitric oxide in the absence of added nitrous oxide.) It can be seen that while the rate of consumption of nitric oxide is decreased, the rate of production of nitrite and hydrogen peroxide remains unaffected, the respective yields being - $G_{(-NO)} = 8.4 \pm 0.7$, $G_{(NO_2^-)} = 6.1 \pm 0.4$ and $G_{(H_2O_2)} = 0.75 \pm 0.2$. The preparation of a whole series of mixtures with various concentrations of nitric oxide and different nitric oxide to nitrous oxide ratios, could not be readily controlled with the above technique, and time did not permit a more thorough investigation of this aspect. However the results of a few experiments in which the nitrous oxide concentration was measured prior to irradiation are shown in Table 17. In these cases the G values quoted are the mean of three separate irradiation experiments per mixture and are subject to approximately ± 7 to 8% error in $G_{(-NO)}$ as above.

TABLE 17

Initial Concentration of N_2O ($\times 10^{-2}$M)	Initial Concentration of NO ($\times 10^{-4}$M)	Mean Concentration of NO ($\times 10^{-4}$M)	Mean Ratio $(NO)/(N_2O)$	$G^z_{(-NO)}$	$G^z_{(NO_2^-)}$
2.16	5.0	4.23	0.0196	9.05	5.93
1.80	7.48	6.28	0.0350	9.59	5.91
1.85	7.07	5.99	0.0324	9.47	5.97
2.12	4.96	4.11	0.0194	8.35	6.00

(b) <u>0.8 N sulphuric acid solutions</u>

Solutions containing mixtures of nitric oxide (4.9 to

6.5×10^{-4}M) and nitrous oxide (approx. 10^{-2}M) were prepared as above but in 0.8N A.R. sulphuric acid. Samples were irradiated such that approximately 40% of the nitric oxide was consumed and subsequently analysed to determine the residual nitric oxide along with the production of nitrite. The consumption of nitric oxide and production of nitrite were found to be linear with dose (Figure 26) with values for the respective yields of $G_{(-NO)} = 15.4 \pm 1.6$, and $G_{(NO_2^-)} = 6.0 \pm 0.2$,

(c) Discussion

The radiation chemistry of nitrous oxide in aqueous solutions over the whole range of pH has been studied by Dainton et al. The results obtained in early studies[77,78] were explicable if the reducing entity in neutral solution (then represented by H) reacted rapidly with nitrous oxide according to

$$H + N_2O = N_2 + OH$$

while the specie present in acid solution, pH 3, (then represented by H_2^+) was incapable of reacting in this manner. These observations are now expressed by the equations[79]

pH $> 4 <$ 11 $\quad H_2O^- + N_2O = N_2 + H_2O + \bar{O}\ (\rightarrow OH)$

pH < 3 $\quad H + N_2O = N_2 + OH$

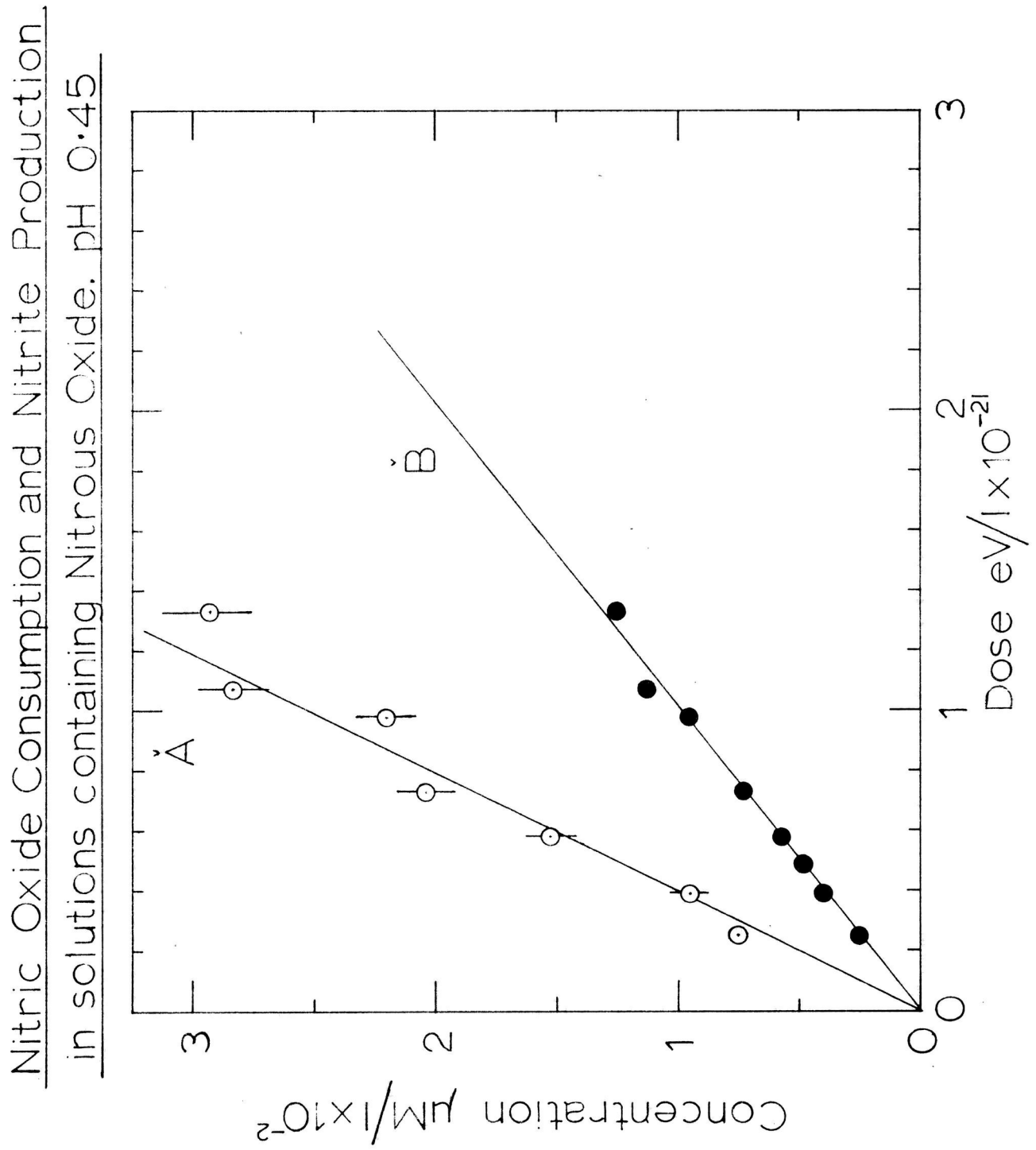
Therefore in solutions of nitric oxide containing nitrous oxide at neutral pH, the following sequence of reactions should occur

$$H_2O = H_2, H_2O_2, OH, H_2O^-$$

$$H_2O^- + NO = HNO + OH^- \quad \ldots\ldots\ldots\ldots (1)$$

$$HNO + NO = N_2O + OH \quad \ldots\ldots\ldots\ldots (3)$$

Figure 26


Nitric Oxide Consumption and Nitrite Production
in solutions containing Nitrous Oxide. pH 0·45
A
B
Concentration μM/l x10⁻²
Dose eV/l x10⁻²¹
0
1
2
3

$$H_2O^- + N_2O = N_2 + H_2O + \bar{O} (\rightarrow OH) \ldots\ (14)$$

$$OH + NO = HNO_2 \ldots\ (5)$$

Here the H_2O^- can also react with N_2O to form an OH radical which then reacts with NO to form nitrite. A kinetic treatment of this reaction scheme shows that the above mechanism predicts the following yields,

$$G^z_{(-NO)} = G^\circ_{(-NO)} - 2\beta G_{H_2O^-} \ldots\ (M)$$

$$G^z_{(NO_2^-)} = G^\circ_{(NO_2^-)} \ldots\ (N)$$

$$G^z_{(N_2O)} = G^\circ_{(N_2O)} - 2\beta G_{H_2O^-} \ldots\ (O)$$

$$G^z_{(N_2)} = \beta G_{H_2O^-} \ldots\ (P)$$

where the parentheses after the letter G^z denote the observed yield of reaction product in the presence of added nitrous oxide at concentration z, G° the corresponding yields in the absence of added nitrous oxide, and

$$\beta = \left[1 + k_1(NO) / k_{14}(N_2O)\right]^{-1}$$

It can be seen that equation (N) predicts that $G^z_{(NO_2^-)}$ is independent of the concentration of nitrous oxide present in solution and should therefore equal $G^\circ_{(NO_2^-)}$, while equation (M) would predict a decrease in $G^z_{(-NO)}$. Both these predictions were observed experimentally (Figure 25 and Table 17) and would appear consistent with the above mechanism involving the simple competition between NO and N_2O for the reducing entity H_2O^-. Rearranging equation (M) we obtain

$$\left[G^\circ_{(-NO)} - G^z_{(-NO)}\right]^{-1} = \frac{1}{2G_{H_2O^-}}\left[1 + k_1(NO)/k_{14}(N_2O)\right] \ldots (Q)$$

Using the values of $G^z_{(-NO)}$ given in Table 17, together with $G^\circ_{(-NO)} = 12.0$, and $G_{H_2O^-} = 2.9$, the reciprocal of equation (Q)

was plotted as a function of the average $(NO)/(N_2O)$ concentrations present during an irradiation (Figure 27). The results conform with this relation and the slope corresponds to a competition constant $k_1 / k_{14} = 40$. However this value does not conform with that deduced from the results of other competitive studies.

Dainton and Peterson[79] have shown that

$$k_{(H_2O^- + N_2O)} / k_{(H_2O^- + H^+)} = 1.25,$$

and Czapski and Allen[83] that

$$k_{(H_2O^- + H^+)} / k_{(H_2O^- + H_2O_2)} \cong k_{(H_2O^- + O_2)} / k_{(H_2O^- + H_2O_2)} = 2.0$$

From these ratios one can infer that

$$k_{(H_2O^- + H^+)} / k_{(H_2O^- + O_2)} = 1 \text{ and}$$
$$k_{(H_2O^- + N_2O)} / k_{(H_2O^- + O_2)} = 1.25.$$

Competitive kinetic studies previously described in this work indicate that

$$k_{(H_2O^- + NO)} / k_{(H_2O^- + O_2)} = 1$$

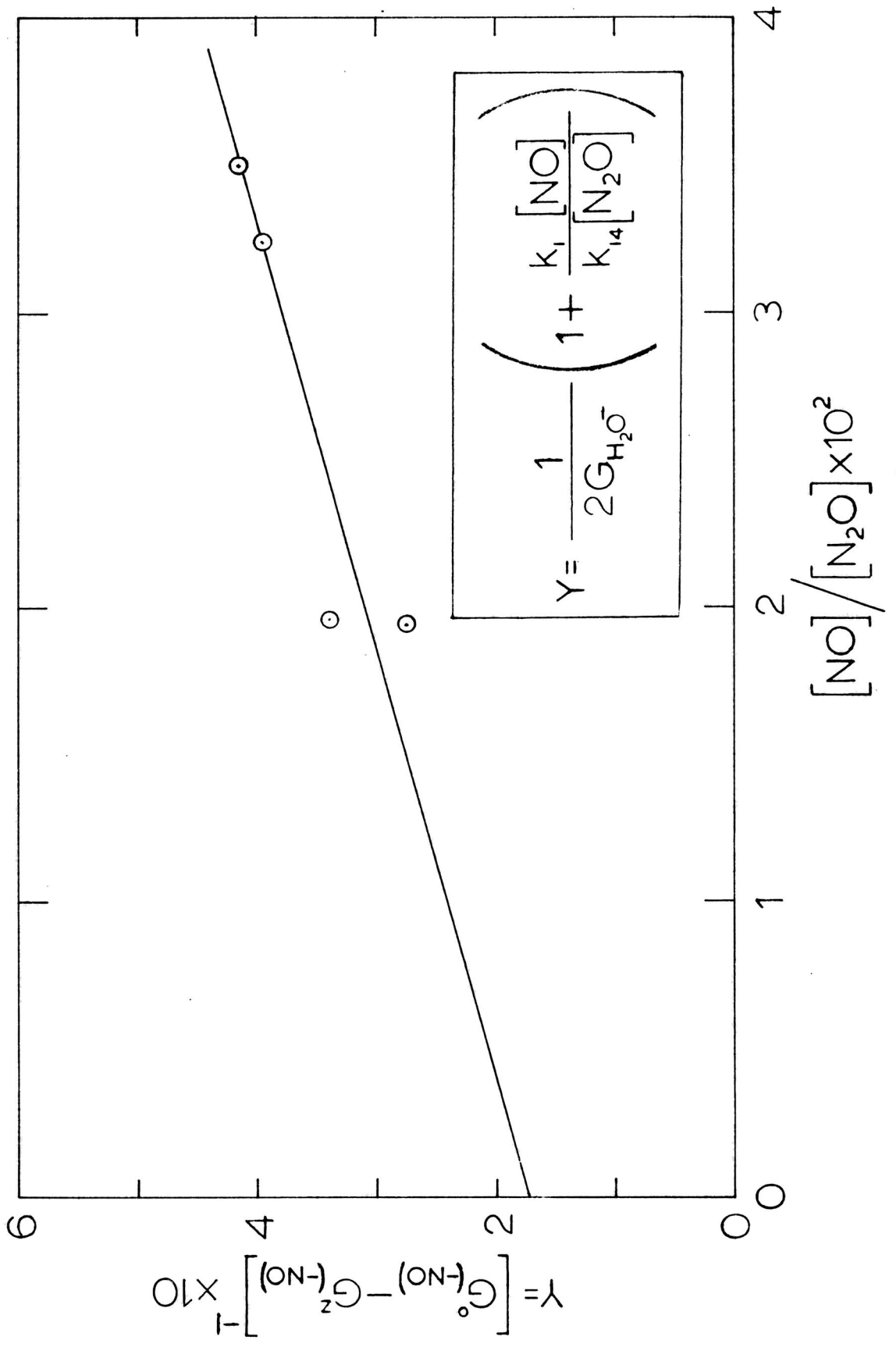
and this suggests that

$$k_{(H_2O^- + NO)} / k_{(H_2O^- + N_2O)} = 1$$

Clearly the experimental value of 40 for the latter competition constant is in marked disagreement with the derived value of approximately 1.0.

In view of the possible analytical errors described previously, the technique adopted in this work did not permit a precise evaluation of this constant but at the same time cannot account for an error of this order of magnitude. Since no special precautions were undertaken to purify the nitrous oxide the possibility of impurities affecting the

Figure 27


$Y = \left[G^{\circ}_{(-NO)} - G^{z}_{(-NO)}\right]^{-1} \times 10$
$Y = \frac{1}{2G_{H_2O^-}}\left(1 + \frac{k_1}{k_{14}}\frac{[NO]}{[N_2O]}\right)$
$[NO]/[N_2O] \times 10^2$
0
1
2
3
4
0
2
4
6

results must be considered. Such interference is difficult to reconcile with the experimental data for two reasons.

(1) The reproducible determinations of $G^{z}_{(NO_2^-)}$ which are found to equal $G^{o}_{(NO_2^-)}$ and are thus in agreement with equation (N).

(2) The results obtained in 0.8N sulphuric acid solution under very similar experimental conditions show that $G^{z}_{(-NO)}$ (15.4 ± 1.4) equals $G^{o}_{(-NO)}$ (15.0 ± 1.0). If it is assumed that the reaction H + NO is rapid, then these results are consistent with the data of Dainton and Peterson[79] and also Czapski and Jortner,[93] that H reacts only slowly with N_2O. This assumption would appear to be justified since the former reaction, as indicated previously, is essentially a radical reaction for which the rate constant will probably be of the order 10^9 litre mole.$^{-1}$ sec.$^{-1}$, while the latter reaction involves bond breakage and has a rate constant about 10^4 litre mole.$^{-1}$ sec.$^{-1}$ [79,93]

The apparent anomaly of the results obtained in neutral solution* is therefore of considerable interest and some alternative mechanism must be invoked to explain these observations.

---

* It should be noted that the maximum concentration of nitrous acid produced in these experiments was 1.4×10^{-4}M which corresponds to a pH of 3.96.

The basis for such a mechanism is suggested from a consideration of the electron affinities of nitric oxide and nitrous oxide. Theoretically one would expect the electron affinity of nitric oxide to be greater than that of nitrous oxide, the former molecule having one unpaired electron, while the latter has only a weak dipole moment. This supposition is apparently substantiated by the early work of Bradbury[94] who studied the formation of negative ions in gases by electron attachment. With nitric oxide a stream of slow electrons readily formed a negative ion, regarded as NO^-, but in contrast similar studies with nitrous oxide showed no such effect, the molecule apparently having no electron affinity. With higher electron energies negative ion formation was observed in nitrous oxide and this was attributed to the dissociative attachment process

$$N_2O + e = N_2 + O^-$$

However it has recently been shown mass spectroscopically by Curran and Fox[95] and Schulz[96] that O^- is formed by electron impact on N_2O with an appearance potential between 0 and 0.05eV and this is attributed to the efficient formation of a temporary negative ion N_2O^-, which subsequently decays into N_2 and O^-. On this basis Dainton and Peterson [79] suggest that N_2O is likely to be an efficient scavenger for the solvated electron and write equation (14) as

$$N_2O + e^-_{aq} = N_2O^-_{aq} \quad \ldots\ldots\ldots\ldots\ldots (15).$$

An equivalent formulation is

$$N_2O_{aq} + H_2O^- = N_2O^-_{aq} + H_2O$$

and (15) must be followed by

$$N_2O^- = N_2 + \bar{O} \text{ (or OH)} \quad \ldots\ldots\ldots \quad (16).$$

Although a precise value for the electron affinity of nitric oxide does not appear to have been established, it is known to be greater than zero[97] and may well compare with the values of 20 and 79 k. cals. mole.$^{-1}$ (exothermic) for oxygen and chlorine dioxide,[97] respectively. Equation (1) is therefore probably more correct when written as

$$H_2O^- + NO = NO^- + H_2O \quad \ldots\ldots\ldots \quad (17)$$

followed by (18) and then (3)

$$NO^- + H^+ = HNO \quad \ldots\ldots\ldots\ldots\ldots \quad (18)$$

or possibly

$$NO^- + NO = N_2O + \bar{O} \quad \ldots\ldots\ldots \quad (19)$$

the overall stoichiometry being the same as (1) and (3).

It is now postulated that the apparent inconsistency between experiment and prediction for the relative rates of reaction of NO and N_2O with the solvated electron can be ascribed to an additional competition between the decomposition of N_2O^- as in (16) (assumed to be first order) and an electron transfer from this complex to nitric oxide, as in

$$N_2O^-_{aq} + NO = NO^- + N_2O \quad \ldots\ldots\ldots \quad (20).$$

This is then followed by (18) or (19) as above. The complete reaction sequence is thus rewritten as

$$H_2O = H_2, H_2O_2, OH, H_2O^-$$

$$H_2O^- + NO = NO^- + H_2O \quad \ldots\ldots\ldots \quad (17)$$

$$NO + H^+ = HNO \quad \ldots\ldots\ldots\ldots\ldots \quad (18)$$

$$HNO + NO = N_2O + OH \quad \ldots\ldots\ldots \quad (3)$$

$$H_2O^- + N_2O = N_2O^- + H_2O \quad \ldots\ldots\ldots \quad (15)$$

$$N_2O^- = N_2 + \bar{O} \ (\rightarrow OH) \quad \ldots\ldots\ldots \quad (16)$$

$$N_2O^- + NO = NO^- + N_2O \quad \ldots\ldots\ldots\ldots \quad (20)$$

$$OH + NO = HNO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

This mechanism predicts that

$$G^z_{(-NO)} = G^\circ_{(-NO)} - 2\alpha'\beta' G_{H_2O^-} \quad \ldots\ldots\ldots\ldots \quad (R)$$

$$G^z_{(NO_2^-)} = G^\circ_{(NO_2^-)}$$

and $$G^z_{(N_2)} = \alpha'\beta' G_{H_2O^-} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (S)$$

where $$\alpha' = \left[1 + k_{17}(NO)/k_{15}(N_2O) \right]^{-1}$$

and $$\beta' = \left[1 + k_{20}(NO)/k_{16} \right]^{-1}$$

Rearranging equations (R) and (S) we have

$$\left[G^\circ_{(-NO)} - G^z_{(-NO)} \right]^{-1} = \frac{1}{2G_{H_2O^-}} \left[1 + k_{17}(NO)/k_{15}(N_2O) \ (1 + k_{20}(NO)/k_{16}) \right] \quad \ldots\ldots\ldots\ldots \quad (T)$$

and

$$\left[G^z_{(N_2)} \right]^{-1} = \frac{1}{G_{H_2O^-}} \left[(1 + k_{17}(NO)/k_{15}(N_2O)(1 + k_{20}(NO)/k_{16}) \right] \quad \ldots\ldots\ldots\ldots \quad (U)$$

Consequently this mechanism could be readily tested by a series of experiments in which

(a) the $(NO)/(N_2O)$ ratio is maintained constant whilst the concentration of NO is varied, and

(b) the concentration of NO is maintained constant and the $(NO)/(N_2O)$ ratio varied.

In the former case a plot of the reciprocal (preferably $\left[G^z_{(N_2)} \right]^{-1}$ for greater accuracy) against the concentration of NO should be a straight line with a slope proportional to $k_{17}\,k_{20} / k_{15}\,k_{16}$ and an intercept equal to

$$1 / G_{H_2O^-} \left[1 + k_{17}(NO)/k_{15}(N_2O) \right]$$

(from equation U). In the latter case a similar reciprocal plot against the $(NO)/(N_2O)$ ratio should also be a straight

line with a slope proportional to $k_{17}\ k_{20} / k_{15}\ k_{16}$ but with an intercept equal to $1 / G_{H_2O^-} \left[1 + k_{20}(NO)\ k_{16} \right]$. The data obtained to date in this work is insufficient to test this hypothesis, but an estimate of k_{20} / k_{16} can be obtained from the results previously presented in Table 17 if it is assumed that $k_{17} = k_{15}$. Using equation (T) and taking $G_{H_2O^-} = 2.9$, then the values for k_{20} / k_{16} deduced in this manner are shown in Table 18

TABLE 18

Mean $(NO)/(N_2O)$	Mean (NO) x 10^4M	$\left[G^{\circ}_{(-NO)} - G^{z}_{(-NO)}\right]^{-1}$	k_{20} / k_{16} mole litre^{-1} x 10^{-3}
0.0196	4.23	0.339	1.88
0.0350	6.28	0.415	2.10
0.0324	5.99	0.395	2.04
0.0194	4.11	0.274	1.36

It would also be expected that other molecules with high electron affinity would behave in a similar manner to that of nitric oxide. Low concentrations of oxygen, and possibly chlorine dioxide, may therefore markedly decrease the yield of nitrogen, $G_{(N_2)}$, obtained from neutral solutions saturated with nitrous oxide.

(6) The irradiation of Nitric Oxide solutions at their Natural pH in the presence of Bromide ion.

In the systems studied so far the added solutes have been shown to compete with the nitric oxide for the solvated electron. A series of experiments were therefore undertaken in the presence of bromide ion which is specific in reacting only with the OH radical.

(a) Results.

Nitric oxide, the concentration of which ranged from 1.2 to 1.84 x 10^{-3}M, was prepared in solutions containing from 10^{-3} to 10^{-1}M bromide ion. All the bromide solutions were prepared using A.R. Potassium Bromide without further purification. Samples were irradiated so that no greater than 40 - 50% of the nitric oxide was consumed and were then analysed for the production of nitrite and hydrogen peroxide, together with the residual nitric oxide. The consumption of nitric oxide and production of nitrite were linear with dose (Figure 28) and the respective yields determined as $G_{(-NO)}$ = 12.7 ± 0.9, and $G_{(NO_2^-)}$ = 6.0 ± 0.2. The average peroxide yield from such solutions was $G_{(H_2O_2)}$ = 0.44 ± 0.08.

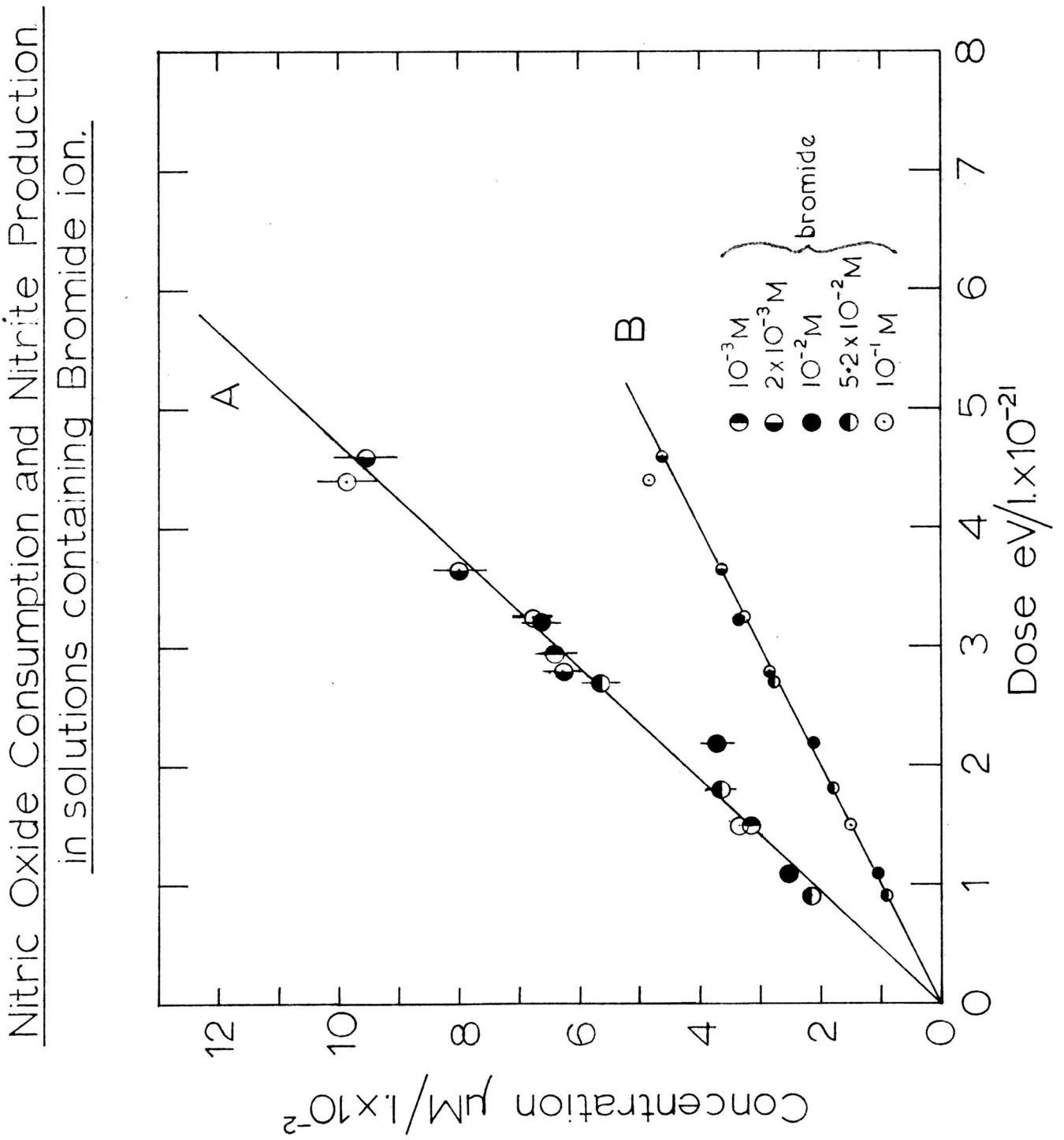
(b) Discussion

In a study of solutions containing bromide ion it has been shown by Sworski,[62] and Allen and Holroyd[63] that the reaction of OH radicals with Br^- is explained by

$$OH + Br^- = Br + OH^- \quad \ldots\ldots\ldots\ldots (21)$$

This reaction is known to be rapid although certain irregularities do exist in the literature with regard to the magnitude of this rate constant.

Figure 28


Nitric Oxide Consumption and Nitrite Production
in solutions containing Bromide ion.
Concentration μM/l.x10⁻²
Dose eV/l.x10⁻²¹
A
B
10⁻³M
2x10⁻³M
10⁻²M
5·2x10⁻²M
10⁻¹M
bromide
0
2
4
6
8
10
12
1
3
5
7

Schwarz and Salzman estimate that

$k_{(OH + Br^-)} / k_{(OH + NO_2^-)} = 0.1$. Combining this value with that of Schwarz and Allen[32] for $k_{(OH + NO_2^-)} / k_{(OH + H_2O_2)} = 55 \pm 20$, together with the absolute value for $k_{(OH + H_2O_2)} = 4.5 \times 10^7$ l. mole.$^{-1}$ sec.$^{-1}$ by Schwarz,[61] we have

$$k_{(OH + Br^-)} = 2.5 \times 10^8 \text{ l. mole.}^{-1} \text{ sec.}^{-1}$$

Ferradini and Koulkes-Pujo[98] have recently studied the competition between Br^- and H_2 for the OH radical. Their results show that

$$k_{(OH + Br^-)} / k_{(OH + H_2)} = 830$$

Using $k_{(OH + H_2)} = 4.5 \times 10^7$ l. mole.$^{-1}$ sec.$^{-1}$,[61] then $k_{(OH + Br^-)} = 3.7 \times 10^{10}$ l. mole.$^{-1}$ sec.$^{-1}$, a value consistent with an independent determination by Burton and Kurien[99] of 1.6×10^{10} l. mole.$^{-1}$ sec.$^{-1}$

These latter values are at about the limit expected for diffusion controlled radical reactions in solution,[100] and if these are taken to be correct then at concentrations of 10^{-3} Br^- this reaction must effectively compete with (5), in solutions containing 10^{-3}M nitric oxide

$$OH + NO = HNO_2 \quad \ldots\ldots\ldots\ldots (5)$$

If the former value is accepted then again irrespective of the magnitude of k_5 some competition would be expected in solutions containing 10^{-1}M Br^- ion. The lack of any decrease in either the nitric oxide or nitrite yields as a function of bromide concentration, suggests that the Br atoms formed in (21) subsequently react in a manner stoichiometrically equivalent to that of OH. A number of reaction sequences consistent with this are indicated below, together with the

relevant enthalpy changes deduced from the data in Table 19.

		ΔH(k.cals.mole^{-1})	
(a)	$OH + Br^- = Br + OH^-$		(21)
	$Br + NO = NOBr$	-24.0	(22)
	$NOBr + NO_2^- = NO_2 + NO + Br^-$	- 0.5	(23)
	$NO_2 + NO + H_2O = 2HNO_2$		(6)
Nett	$OH + NO = HNO_2$		
(b)	$OH + Br^- = Br + OH^-$		(21)
	$Br + NO_2^- = Br^- + NO_2$	-24.5	(24)
	$NO_2 + NO + H_2O = 2HNO_2$		(6)
Nett	$OH + NO = HNO_2$		
(c)	$OH + Br^- = Br + OH^-$		(21)
	$Br + NO = NOBr$		(22)
	$NOBr + H_2O = 2H^+ + Br^- + NO_2^-$	- 3.0	(25)
Nett	$OH + NO = HNO_2$		

As all the reactions are thermochemically feasible an absolute discrimination cannot be made on purely energetic grounds, but of sequences (a) and (b), the latter would appear the more favourable. Since the initial concentration of nitric oxide in the solution greatly exceeds that of the nitrite ion it would appear that scheme (c), based on the simple hydrolysis of NOBr is the more likely mechanism, although a contribution from (b) may become of increasing importance as the $(NO_2^-)/(NO)$ ratio in the solution increases.

No measure of k_5 / k_{21} can be obtained from this system and a similar study with chloride ion which reacts in acid solution as in (26)[101]

TABLE 19

Species	Reference Number	Heat of formation (gaseous)	Heat of solution	Heat of formation (aqueous)
Br	56	26.7	-2.7 *	24.0
HBr	"	- 8.66		-28.9
Br^-	"			-28.9
NOBr	"	19.6	-2.6 *	17.0
Cl	"	29.0	-3.0 *	26.0
HCl	"	-22.06		-40.0
Cl^-	"			-40.0
NOCl	"	12.6	-2.6 *	10.0
NO	"	21.6	-4.6 *	17.0
NO_2	"	8.1	-5.1 *	3.0
NO_2^-	"			-25.4
H^+	"	52.1		0.0
H_2O	55	-57.8	-10.5	-68.3

* Assumed values.

$$H^+ + Cl^- + OH = Cl + H_2O \quad \ldots\ldots\ldots\ldots \quad (26)$$

was not undertaken since the thermochemical data for Cl, appertaining to the reactions (22) to (25), indicated no major difference in energetics from that of Br. The corresponding enthalpy values deduced from the data in Table 19 are -33.0, -4.6, -37.6 and-7.1 k. cals./mole. for reactions (22) to (25), respectively. An alternative competing solute must therefore be sought to enable information relative to the rate of reaction (5) to be ascertained. From a study of aqueous oxygenated solutions of ethanol containing bromide ion Hummel and Allen[11] deduce

$$k_{(OH + Br^-)} / k_{(OH + C_2H_5OH)} = 0.6$$

A similar study using solutions of ethanol and nitric oxide may furnish data relevant to $k_{(OH + NO)} / k_{(OH + C_2H_5OH)}$. Alternatively it may be possible to study the competition between nitric oxide and hydrogen for the OH radical and thus obtain the competition constant $k_{(OH + NO)} / k_{(OH + H_2)}$.

CHAPTER VI

RADIOBIOLOGICAL IMPLICATIONS; FUTURE WORK AND SUMMARY

Significance of this work with regard to radiobiology

It has previously been indicated that both nitric oxide and oxygen markedly enhance the sensitivity of a variety of "wet" cells and tissues to the action of ionising radiation. The enhancement by oxygen of ionising radiation effects on living cells has been recognised for many years,[102] while the evidence for the equivalent role of nitric oxide is of comparatively recent origin.[22] Both effects are however unique in so far as no other gas under ordinary circumstances has been found to behave in a similar manner. Clearly the mechanism whereby these gases exert their effect is of importance for the understanding of the various processes which occur on the absorption of energy in a living cell. No attempt will be made here to give a comprehensive survey of the various mechanisms which have been proposed to account for the oxygen effect, as such considerations are adequately expressed elsewhere.[20,21] However a concise account of current ideas and a comment on the relevance of the present radiation chemical data for solutions of nitric oxide is presented below.

The role of oxygen and nitric oxide in modifying the radiosensitivity of biological substrates.

It has been common to express the role of oxygen in terms of its interaction with the reducing radical "H" to form $HO_2^{\cdot}$, followed by further oxidative processes via $HO_2^{\cdot}$. This mechanism was originally proposed by Gray[103] and was based on a comparison with the apparently analogous situation

in radiation chemistry with respect to the increased yield of ferric ion from oxygenated solutions of ferrous sulphate. This view is now regarded as most unlikely and cogent arguments to this effect are discussed by Alper[19,104] and Gray.[20] Furthermore the short mean diffusion path of 30 Angstroms (A) for "H" atoms in yeast cells led Hutchinson[105] to doubt that any $HO_2^{\cdot}$ was formed at all in a living cell; the oxygen molecules in aerated water being some 180A apart.

Alper and Howard Flanders[104] were the first to obtain a precise relation between the environmental concentration of oxygen and the radiosensitivity of bacteria, the experimental data fitting a curve represented by the equation

$$\text{Relative sensitivity } \frac{S}{S_N} = \frac{m(O_2) + K}{(O_2) + K} \quad \ldots\ldots\ldots\ldots\ldots (1)$$

where S_N is the radiosensitivity in the absence of oxygen; (O_2) is the oxygen concentration in μ M/l; S is the radiosensitivity at an oxygen concentration (O_2); K, expressed as an oxygen concentration, is that concentration at which the sensitivity is midway between the maximum and minimum values it assumes for anoxic and well-oxygenated solutions, respectively, and m is the maximum enhancement ratio at high concentrations of oxygen, i.e. $m = S_{max} / S_N$ where S_{max} is the maximum radiosensitivity. Later, Flanders and Jockey[25] were able to establish an identical dependence for the radiosensitivity of bacteria on the concentration of nitric oxide.

A relation of this type between concentration and sensitivity indicated that simple competitive kinetics were applicable to both gases and appears to be best explained in

terms of the hypothesis originally suggested by Alper and Flanders,[104] latterly extended by Flanders and Moore.[106] These workers postulate that the action of radiation, whether directly, or indirectly through radical intermediates, produces concurrently in some vital molecule R, two forms of damage:- (i) A permanent irreversible injury R^1, and (ii) a short lived reversible injury regarded as a free radical R·, the fate of which depends on whether R·can repair itself to R or other undetectable forms of injury, or alternatively reacts with oxygen or nitric oxide to form RO_2· or RNO, respectively, both of which are incapable of restoration to R. These alternatives can be conveniently represented by the equations

$$R \longrightarrow R^1 \text{ (lethal injury)}$$

$$R \longrightarrow R\cdot$$

$$R\cdot \xrightarrow{k_1} R \text{ (repair)} \quad \ldots\ldots\ldots\ldots\ldots (1)$$

$$\underset{(NO)}{R\cdot + O_2} \xrightarrow{k_2} \underset{(RNO)}{RO_2\cdot} \text{ (lethal)} \quad \ldots\ldots\ldots\ldots\ldots (2)$$

On this basis the oxygen (or nitric oxide) dependent fraction of the radiation induced injury can be expressed in terms of the competition between reactions (1) and (2).

If G_{R1} represents the yield of R^1, $G_{R\cdot}$ the yield of R·, and G_T the total yield of damage in the presence of oxygen or nitric oxide at concentration (X), then

$$G_T = G_{R1} + G_{R\cdot}\, k_2(X) / k_1 + k_2(X)$$

Assuming the relative proportion of $G_{R1} / G_{R\cdot} = 1/(m-1)$ then

$$\frac{G_T - G_{R1}}{G_{R1}} = \frac{(m-1)\,(X)}{K + (X)}$$

which on equating G_T with S, and G_{R1} with S_N and rearranging becomes

$$\frac{S}{S_N} = \frac{m(X) + K}{(X) + K}$$

where $K = k_1 / k_2$.

This equation is clearly identical with equation (1) above but is significant in that the K value can now be interpreted as the ratio of the rates of the reactions (1) and (2).

On the basis of this mechanism the identical values observed for K of 1.6 μM/l for both oxygen and nitric oxide,[25] indicates that both these gases react equally rapidly with the radical R·. This cannot be confirmed from the data presented in this thesis but an indication to this effect may be drawn from the observation that $k_{(H_2O^- + O_2)} \cong k_{(H_2O^- + NO)}$. It may be possible in future work to obtain data which will be of more direct application to radiobiology, such as a measure of the relative rates of reaction of some organic radical with both nitric oxide and oxygen.

Future Work

It is apparent from the limited data presented in this thesis that very definite possibilities exist in aqueous radiation chemistry for the further application of the nitric oxide system. A number of avenues for further research have already been indicated in the text and these together with several additional suggestions are briefly indicated below.

(1) Experimentally there is room for an improvement in the analytical technique, especially in the analyses for nitric oxide. A clip could be designed to accurately control the volume of solution ejected from a syringe and subsequent analyses for nitric oxide, via gas chromatography, would considerably improve this aspect.

(2) A more accurate study of the nitric oxide - nitrite competition in neutral solution via measurements of the nitrous oxide yield, $G^{x}_{(N_2O)}$, would enable a more precise value of the relation $k_{(H_2O^- + NO)}$ to $k_{(H_2O^- + O_2)}$ to be ascertained. At the same time the composition of the yield of reducing entity could be compared with that established for oxygenated solutions.

A repeat of this competition in acid solution should provide information relative to the competition constant $k_{(H + NO)} / k_{(H + HONO)}$, while a study in neutral solution using atomic hydrogen should elucidate $k_{(H + NO)} / k_{(H + NO_2^-)}$.

(3) Competitive studies with mixtures of nitric oxide and hydrogen peroxide in neutral and acid solution, when the respective competing reactions are

$$H_2O^- + NO = NO^- + H_2O$$
$$H_2O^- + H_2O_2 = H_2O + OH^- + OH$$ } neutral

and

$$H + NO = HNO$$
$$H + H_2O_2 = H_2O + OH$$ } acid

may furnish the competition constants $k_{(H_2O^- + NO)} / k_{(H_2O^- + H_2O_2)}$ and $k_{(H + NO)} / k_{(H + H_2O_2)}$, respectively, which could then be correlated with those already established for oxygen.

(4) A thorough investigation should be made of the nitric oxide - nitrous oxide system over a wide concentration, and suitably buffered pH range, to test the postulated mechanism for mixtures of these two solutes. A similar correlative study with mixtures of oxygen and nitrous oxide would be of value.

(5) The determination of competition constants relative to the OH radical and nitric oxide would be of interest. Kinetic studies with mixtures of ethanol (or hydrogen) and nitric oxide when the respective competing reactions are

$$OH + NO = HNO_2$$
$$OH + CH_3CH_2OH = H_2O + \cdot CH_2CH_2OH$$
$$OH + H_2 = H + H_2O$$

may establish the ratios $k_{(OH + NO)} / k_{(OH + C_2H_5OH)}$ or $k_{(OH + NO)} / k_{(OH + H_2)}$.

(6) No studies have yet been made with alkaline solutions of nitric oxide. Such experiments might be undertaken to confirm the increase in yield of the primary radical species with increase in pH. A limiting factor may arise here as a result of the thermal reaction

$$4OH^- + 6NO = 4NO_2^- + N_2 + 2H_2O.$$

Summary

Aqueous oxygen free solutions of nitric oxide were irradiated with Co^{60} γ rays and then analysed for NO_2^-, NO_3^-, N_2O, N_2, H_2O_2 and H_2 together with the residual NO. At pH approximately 3.5 to 4.0, the product yields were $G_{(NO_2^-)} = 5.9_5 \pm 0.2$ molecules per 100 eV, $G_{(N_2O)} = 3.1 \pm 0.1_5$, while $G_{(-NO)} = 12.0 \pm 0.8$. No NO_3^- or N_2 was observed and $G_{(H_2O_2)} = 0.52 \pm 0.05$ while $G_{(H_2)} = 0.40$. These yields increase with increasing acidity to the values $G_{(NO_2^-)} = 6.5 \pm 0.2$, and $G_{(-NO)} = 15.0 \pm 1.0$, at pH 0.45. The results conform with the following mechanism:

$$H_2O = H_2, H_2O_2, OH, \underline{H}$$

$$\underline{H} + NO = HNO \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$HNO + NO = N_2O + OH \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

$$OH + NO = HNO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where $\underline{H}$ represents the reducing entities H_2O^-, or H, in neutral and acid solution, respectively. Reaction (3) is exothermic since the dissociation energy of the H - NO bond is 48 k. cals. This mechanism requires that $G_{(-NO)} = 3G_{\underline{H}} + G_{OH}$; $G_{(NO_2^-)} = G_{\underline{H}} + G_{OH}$, and $G_{(N_2O)} = G_{\underline{H}}$. These relations agree well with the observed results if one adopts accepted values for $G_{\underline{H}}$ and G_{OH} at the appropriate pH. At neutral pH more precise agreement is obtained if contributions of $2\left[G_{H_2} - G_{(H_2)}\right]$, and $2\left[G_{H_2O_2} - G_{(H_2O_2)}\right]$, (attributed to radical scavenging by NO) are added to $G_{\underline{H}}$ and G_{OH}, respectively, these corrected radical yields accounting for the decrease in the molecular product yields $G_{(H_2)}$, and

$G_{(H_2O_2)}$, in comparison with their accepted values G_{H_2} and $G_{H_2O_2}$.

The mechanism has been confirmed by competitive studies in the presence of added NO_2^-. The reaction of H_2O^- with NO_2^- to form NO + $2OH^-$, has been shown to proceed with a rate constant $k_{(H_2O^- + NO_2^-)}$, which is 4.7 times smaller than $k_{(H_2O^- + NO)}$. From this value it is inferred that $k_{(H_2O^- + NO)}$ approximately equals $k_{(H_2O^- + O_2)}$. Studies on the influence of added N_2O indicate that $k_{(H_2O^- + NO)} / k_{(H_2O^- + N_2O)}$ approximately equals 40; in marked disagreement with the approximate value of 1, derived from the results of other workers. A mechanism is suggested to account for this anomalous result without excluding the possibility that $k_{(H_2O^- + NO)}$ equals $k_{(H_2O^- + N_2O)}$. The results of experiments in the presence of Br^- indicate that the Br atom formed by

$$OH + Br^- = Br + OH^-$$

reacts in a manner stoichiometrically equivalent to that of OH in reaction (5) above. Mechanisms consistent with this view are discussed, but cannot provide data relative to $k_{(OH + NO)}$.

The results may have some significance in interpreting the similar radiobiological effects of NO and O_2.

APPENDICES I, II, III and IV

Appendix I

Dosimetry.

The calculation of the dose rate from the ferric ion oxidation yields.

(a) **eV/l/hour**

Using the 30 Curie Co^{60} source a solution of 10^{-3}M $FeSO_4$ and 10^{-3}M NaCl in 0.8N H_2SO_4 was oxidised at the rate of 305.2 μM/l/hour.

i.e. $3.052 \times 10^{-4} \times 6.023 \times 10^{23}$ molecules /l/hr.

$G_{(Fe^{3+})}$ = 15.5 molecules / 100eV

$\therefore$ Dose rate = $\frac{3.052 \times 10^{-4} \times 6.023 \times 10^{23} \times 100}{15.5}$ eV/l/hr.

= 1.184×10^{21} eV/l/hr.

(b) k.rads./hr.

1 rad = 100 ergs/gm.

$\therefore$ 1 kilo rad = $100 \times 10^6 \rho$ ergs/l = $10^8 \rho$ ergs/l.

where ρ = the density of the solution.

1eV = 1.6×10^{-12} ergs

$\therefore$ 1 k. rad = $\frac{10^8 \rho}{1.6 \times 10^{-12}}$ eV/l.

= $6.24 \rho \times 10^{19}$ eV/l.

Dose rate in k. rads = $\frac{1.184 \times 10^{21}}{6.24 \times 1.025 \times 10^{19}}$ = 18.5 k.rads/hr.

where ρ for 0.8N H_2SO_4 = 1.025

Appendix II

The derivation of the reaction kinetics for solutions containing nitric oxide and nitrite ion

The derivation of the reaction kinetics for this system is shown here in more detail to serve as a typical example of the procedure adopted throughout in this thesis.

The reaction sequence is as follows,

$$H_2O = H_2, H_2O_2, OH, H_2O^-$$

$$(1-\alpha)H_2O^- + NO = HNO + OH^- \quad \ldots\ldots\ldots\ldots\ldots (1)$$

$$HNO + NO = N_2O + OH \quad \ldots\ldots\ldots\ldots\ldots (3)$$

$$\alpha\, H_2O^- + NO_2^- = NO + 2OH^- \quad \ldots\ldots\ldots\ldots\ldots (4)$$

$$(1-\beta)\, OH + NO = HNO_2 \quad \ldots\ldots\ldots\ldots\ldots (5)$$

$$\beta\, OH + NO_2^- = NO_2 + OH^- \quad \ldots\ldots\ldots\ldots\ldots (6)$$

$$NO_2 + NO + H_2O = 2HNO_2 \quad \ldots\ldots\ldots\ldots\ldots (7)$$

If α represents the fraction of solvated electrons reacting with nitrite ion, then $(1-\alpha)$ will react with nitric oxide. Similarly if β represents the fraction of OH radicals reacting with nitrite ion, then $(1-\beta)$ will react with nitric oxide. Derived yields in the presence of nitrite ion at concentration x, are represented by placing the formula in parentheses after the symbol G^x, as $G^x_{(NO_2^-)}$. In the absence of added nitrite ion, such yields are represented by the symbol G°, as $G^\circ_{(NO_2^-)}$.

Therefore

$$G^x_{(-NO)} = 2(1-\alpha)G_{H_2O^-} - \alpha G_{H_2O^-} + (1-\beta)\left[G_{OH} + (1-\alpha)G_{H_2O^-}\right] + \beta\left[G_{OH} + (1-\alpha)G_{H_2O^-}\right]$$

$$= 3G_{H_2O^-} + G_{OH} - 4\alpha G_{H_2O^-}$$

$$= G^\circ_{(-NO)} - 4\alpha G_{H_2O^-} \quad \ldots\ldots\ldots\ldots\ldots (A)$$

where $\alpha = k_4(NO_2^-) / k_4(NO_2^-) + k_1(NO)$

$= \left[1 + k_1(NO) / k_4(NO_2^-)\right]^{-1}$

Similarly

$$G^x_{(NO_2^-)} = G_{H_2O^-} + G_{OH} - 2\alpha G_{H_2O^-}$$

$$= G^\circ_{(NO_2^-)} - 2\alpha G_{H_2O^-} \quad \ldots\ldots\ldots\ldots\ldots (B)$$

and

$$G^x_{(N_2O)} = G_{H_2O^-} - \alpha G_{H_2O^-}$$

$$= G^\circ_{(N_2O)} - \alpha G_{H_2O^-} \quad \ldots\ldots\ldots\ldots\ldots (C)$$

Appendix III

Integration of the equations (A), (B) and (C)

Consider first the case of equation B. Substituting the values $G^{\circ}_{(NO_2^-)} = 5.9_5$, $G_{H_2O^-} = 2.9$, and $k_1/k_4 = 4.7$ then

$$G^{x}_{(NO_2^-)} = 5.9_5 - \frac{5.8}{1 + 4.7(NO)/NO_2^-)}$$

The rate of formation of nitrite at any instant is then given by

$$\frac{d(NO_2^-)}{d(dose)} = a - \frac{2g}{1 + 4.7(NO)/(NO_2^-)}$$

where $a = 5.9_5$, and $g = 2.9$.

Letting $y = (NO)$, $x = (NO_2^-)$, $t = (dose)$ and $K = 4.7$ then

$$\frac{dx}{dt} = a - \frac{2g}{1 + Ky/x}$$

From the experimental observations in the absence of added nitrite ion it is evident that to a first approximation

$$y = P - qx$$

where P = the initial concentration of nitric oxide, and

$$q = G^{\circ}_{(-NO)} / G^{\circ}_{(NO_2^-)} = 12.0 / 5.9 = 2.034$$

$$\therefore \frac{dx}{dt} = a - \frac{2g}{1 + K(P-qx)/x}$$

$$\therefore \frac{dx}{dt} = a - \frac{2g}{(1-Kq) + KP/x}$$

Substituting $K' = (1-Kq)$ and $K'' = KP$ and rearranging, then

$$dt = \frac{dx}{a - 2gx/K'x + K''}$$

$$\therefore dt = \frac{dx(K'x + K'')}{x(aK' - 2g) + aK''}$$

Substituting $A = (aK' - 2g)$ and $B = aK''$ and integrating knowing that when $t = 0$, $x = 0$, we have

$$\int dt = \int \frac{K'x\,dx}{Ax + B} + \int \frac{K''dx}{Ax + B}$$

$$\therefore t = \frac{K'x}{A} - \left[\frac{K'}{A}\left(\frac{B}{A} - \frac{K''}{K'}\right) \ln \frac{(Ax + B)}{B}\right] \quad \ldots\ (K')$$

Evaluating the constants we obtain

$$\frac{t}{P} = 0.151\frac{x}{P} - 8.409 \times 10^{-3} \ln(-2.032\frac{x}{P} + 1) \quad \ldots\ (K)$$

Considering now equations (A) and (C) respectively, we have initially for (A),

$$-\frac{dy}{dt} = a' - \frac{4g}{1 + Ky/(P-y)/q}$$

where $a' = G^{\circ}_{(-NO)} = 12.0$.

Rearranging we have

$$-\frac{dy}{dt} = \frac{A'y + B'}{Cy + P}$$

where $A' = a'(qK-1) + 4g$, $B' = (a'P - 4gP)$, and $C = (qK-1)$.

Integrating with the condition that $y = P$ when $t = 0$, we obtain

$$t = \frac{CP}{A'} - \frac{Cy}{A'} - \frac{(PA' - B'C)}{(A')^2} \ln \frac{(A'y + B')}{(A'P + B')} \quad \ldots\ (J')$$

and evaluating the constants this becomes

$$\frac{t}{P} = 7.484 \times 10^{-2} - 7.484 \times 10^{-2}\frac{y}{P} - 8.474 \times 10^{-3} \ln\left(\frac{114.4y + 0.4P}{114.4P + 0.4P}\right) \quad \ldots\ (J)$$

For (C) we have initially

$$\frac{dz}{dt} = a'' - \frac{g}{1 + K(P-fqz)/fz}$$

where $z = (N_2O)$, $a'' = G^{\circ}_{(N_2O)} = 3.1$, and $f = G^{\circ}_{(NO_2^-)} / G^{\circ}_{(N_2O)} \cong 2.0$

Rearranging we have

$$\frac{dz}{dt} = a'' - \frac{fgz}{K^{\circ}z + K''}$$

where $K^{\circ} = f(1-Kq)$ and $K'' = KP$.

Integrating with the condition that $z = 0$, when $t = 0$,

we obtain

$$t = \frac{K^{\circ}z}{A''} - \left[\frac{K^{\circ}}{A''}\left(\frac{B}{A''} - \frac{K''}{K^{\circ}}\right) \ln \frac{(A''z + B)}{B} \right] \ldots\ldots (L')$$

where $A'' = (a''K^{\circ}-fg)$ and $B = a''K''$.

Evaluating the constants we obtain

$$\frac{t}{P} = \frac{0.2908z}{P} - 7.881 \times 10^{-3} \ln\left(\frac{-4.041z}{P} + 1\right) \ldots(L)$$

Appendix IV

Considering the integrated but non expanded form of equation (B) we have equation (K)

$$t = \frac{K'x}{A} - \left[\frac{K'}{A}\left(\frac{B}{A} - \frac{K''}{K'}\right) \ln \frac{(Ax + B)}{B}\right] \quad \ldots\ldots\ldots (K')$$

Expanding the logarithmic term in this integral, taking the first term only, we have

$\ln(1 + Ax/B)$ approximately equals Ax/B.

$$\therefore t = \frac{K'x}{A} - \left[\frac{K'}{A}\left(\frac{B}{A} - \frac{K''}{K'}\right)\frac{Ax}{B}\right]$$

$$= \frac{K''x}{B} \quad \text{i.e.} \quad x = \frac{Bt}{K''}$$

Substituting $B = aK''$, and $a = G^{\circ}_{(NO_2^-)}$, we have

$$x = G^{\circ}_{(NO_2^-)}t$$

Expanding the logarithmic term to include the second term we have

$$\ln(1 + Ax/B) = Ax/B - A^2x^2/2B^2 +$$

$$\therefore t = \frac{K'x^2}{2B} + \frac{K''x}{B} - \frac{K''Ax^2}{2B^2}$$

Rearranging this becomes

$$\frac{Bt}{K''} = G^{\circ}_{(NO_2^-)}t = x + \frac{x^2}{2}\left[\frac{K'}{K''} - \frac{A}{B}\right]$$

Evaluating the constants we then obtain

$$G^{\circ}_{(NO_2^-)}t = x + \frac{x^2 . G_{H_2O^-}}{G^{\circ}_{(NO_2^-)} . k_1P/k_4}$$

$$G^{\circ}_{(NO_2^-)}t = x + \frac{x^2}{P} . 0.104$$

REFERENCES

References

(1) LIND, S.C. The Chemical Effects of Alpha Particles and Electrons. Chemical Catalog. Co. Inc. (1928).

(2) FRICKE, H. and MORSE, S. Phil. Mag. 7, (1929) p.129.

(3) Radn. Res. 17, (1962) p.253.

(4) ALLEN, A.O. The Radiation Chemistry of Water and Aqueous Solutions. D. Van Nostrand Co. Inc. (1961).

(5) HART, E.J. and PLATZMAN, R.L. Mechanisms in Radiobiology. Acad. Press, Vol. I, (1961) p.93.

(6) MILLER, N. Rev. Pure and App. Chem. Royal Aust. Chem. Inst. 7, (1957) p.123.

(7) BACQ, Z.M. and ALEXANDER, P. Fundamentals of Radiobiology. Butterworths Scientific Publications (1955).

(8) JOHNS, H.E. and LAUGHLIN, J.S. Radiation Dosimetry, p.50. Eds. Hine and Brownell. Acad. Press (1956).

(9) WEISS, J. Nature 153, (1944) p.749.

(10) HOCHANADEL, C.J. Radn. Res. 17, (1962) p.286.

(11) HUMMEL, A. and ALLEN, A.O. Radn. Res. 17, (1962) p.302.

(12) PLATZMAN, R.L. Second Int. Congress of Radn. Res., Harrogate, Aug. 5-11, (1962). Abstracts of Papers, p.128.

(13) PLATZMAN, R.L. Radn. Res. 17, (1962) p.419.

(14) DAINTON, F.S. Radn. Res., Supplement 1, (1959) p.1.

(15) LEA, D.E. Actions of ionising Radiations on Living Cells. Camb. Univ. Press (1946).

(16) PLATZMAN, R.L. See reference (14) and Ann. Rev. Phys. Chem. 11, (1960) p.95.

(17) SAMUEL, A.H. and MAGEE, J.L. J. Chem. Phys. 21, (1953), p.1080.

(18) KUPPERMAN, A. Actions Chimiques et Biol. des Radiations, (M. Haissinsky, Ed.) Vol. 5, p.87. Acad. Press (1961).

(19) ALPER, T. (a) Radn. Res. 5, (1956) p.573.
(b) Mechanisms in radiobiology, Vol. I, p.353. Acad. Press Inc. (1961).

(20) GRAY, L.H. Radn. Biol. Proc. of 2nd Aust. Conf. on Rad. Biol., 15-18 Dec. (1958) p.152. Ed. J. Martin. Butterworths.

(21) GRAY, L.H. Lectures on the Scientific Basis of Medicine, Vol. VII, (1957-58) p.315. Athlone Press.

(22) HOWARD-FLANDERS, P. Nature 180, (1957) p.1191.

(23) KILHMAN, B.A. Exp. Cell Res. 14, (1958) p.639.

(24) GRAY, L.H., GREEN, F.O. and HAWES, C.A. Nature 182, (1958) p.952.

(25) HOWARD-FLANDERS, P. and JOCKEY, P. Radn. Res. 13, (1960) p.466.

(26) POWERS, E.L. et al. Radn. Res. 11, (1959) p.461.

(27) SPARRMAN, B. et al. Acta. Chem. Scand. 13, (1959) p.199.

(28) BLANCHARD, A.A. Inorganic Syntheses, Vol. II, p.126.

(29) HERSCH, P.A. Anal. Chem. 32, (1960) p.1030.

(30) WILKINSON, J. Ph.D. Thesis. University of Edinburgh, (1952).

(31) SHINN, M.B. Ind. & Eng. Chem. Anal. Edn. 13, (1941) p.33.

(32) SCHWARZ, H.A. and ALLEN, A.O. J.A.C.S. 77, (1955) p.1324.

(33) WAYNE, L.G. and YOST, D.M. J. Chem. Phys. 18, (1950) p.767.

(34) VOGEL, A.I. A text book of Quantitative Inorganic Analysis. 2nd Editn. Longmans. p.870.

(35) SNELL, F.D. and SNELL, T. Colorimetric Methods of Analysis, 3rd Edn., Vol. II, (1949) p.792. D. Van Nostrand.

(36) GHORMLEY, J.A. et al. (a) J. Phys. Chem. 56, (1952) p.575.
(b) J. Phys. Chem. 56, (1952) p.587.

(37) AWTREY, A.D. and CONNICK, R.E. J.A.C.S. 73, (1951) p.1842.

(38) GRAVEN, W.M. Anal. Chem. 31 (7), (1959) p.1197.

(39) HOCHANADEL, C.J. and GHORMLEY, J.A. Radn. Res. 3, (1955) p.227.

(40) VOGEL, A.I. A text book of Quantitative Inorganic Analysis. 2nd Edn. p.7.

(41) WEISS, J. Ann. Reps. XLIV, (1947) p.60.

(42) SMALLWOOD, H.M. J.A.C.S. 51^2, (1929) p.1985.

(43) BLACKMORE, D.R. and HINSHELWOOD, C. Proc. Roy. Soc. 268A, (1962) pp.21 and 36.

(44) WOJCIECHOWSKI, B.W. and LAIDLER, K.J. (a) Can. J. Chem. 38 (1960) p.1027. (b) Proc. Roy. Soc. 260, (1961) p.103. (c) Proc. Roy. Soc. 270, (1962) p.254.

(45) HARTECK, P. Ber. Deut. Chem. 66, (1933) p.423.

(46) DALBY, F.W. Can. J. Phys. 36, (1958), p.1336.

(47) HIRSCHLAFF and NORRISH. J. Chem. Soc. (1936) p.1580.

(48) BROWN, H.W. and PIMENTEL, G.C. J. Chem. Phys. 29, (1958) p.883.

(49) ROBINSON, G.W. and McCARTY, M. J. Chem. Phys. 28, (1958) p.350. Can. J. Phys. 36, (1958), p.1590.

(50) CASHION, J.K. and POLANYI, J.C. J. Chem. Phys. 30, (1959) p.317.

(51) CLEMENT, M.J.Y. and RAMSAY, D.A. Can. J. Phys. 39, (1961) p.205.

(52) BANCROFT, J.L. et al. Can. J. Phys. 40, (1962) p.322.

(53) CLYNE, M.A.A. and THRUSH, B.A. Trans. F. Soc. 57, (1961) p.1305.

(54) CLYNE, M.A.A. and THRUSH, B.A. Disc. F. Soc., Cambridge, April, (1962) Proof 14.

(55) GRAY, P. Trans. F. Soc. 55, (1959) p.408.

(56) Circular of Nat. Bur. Stds. Selected Values of Chemical Thermodynamic Properties.

(57) BICHOWSKY and ROSSINI. Thermochemistry of Chemical Substances. Reinhold Pub., (1936) p.32.

(58) KELLY, P. and SMITH, M. J. Chem. Soc., $(1961)^2$ pp.1479 & 1487.

(59) ASHMORE, P.G. Disc. F. Soc. Cambridge, April 12th (1962). Informal disc. on inhibition reactions with nitric oxide.

(60) TYLER, B.J. Nature 195, (1962) p.279.

(61) SCHWARZ, H.A. J. Phys. Chem., 66, (1962) p.255.

(62) SWORSKI, T.J. J.A.C.S. 76, (1954) p.4687.

(63) ALLEN, A.O. and HOLROYD, R.A. J.A.C.S. 77, (1955) p.5852.

(64) SCHWARZ, H.A. J.A.C.S. 77, (1955) p.4960.

(65) SCHWARZ, H.A. and SALZMAN, A.J. Radn. Res. 9, (1958) p.502.

(66) BAXENDALE, J.H. and HUGHES, G. Z. Phys. Chem. 14, (1958) pp.306,323.

(67) WEISS, J. Nature,186, (1960) p.751.

(68) RIGG, T., STEIN, G. and WEISS, J. Proc. Roy. Soc. 211, (1952) p.375.

(69) RIGG, T. and WEISS, J. J.C.S., $(1952)_4$ p.4198.

(70) HALPERN, J. et al. Nature 186, (1960) p.629.

(71) CZAPSKI, G. et al. J. Phys. Chem. 65, (1961) p.960.

(72) BARR, N.F. and ALLEN, A.O. J. Phys. Chem. 63, (1959) p.928.

(73) DAINTON, F.S. et al. Trans. F. Soc. 55, (1959) p.1761.

(74) CZAPSKI, G. et al. J. Phys. Chem. 65, (1961) p.964.

(75) ALLAN, J.T. and SCHOLES, G. Nature 187, (1960) p.218.

(76) HAYON, E. and ALLEN, A.O. J. Phys. Chem. 65, (1961) p.2181.

(77) DAINTON, F.S. and PETERSON, D.B. Nature 186, (1960) p.878.

(78) DAINTON, F.S. and SILLS, S.A. Nature 186, (1960) p.879.

(79) DAINTON, F.S. and PETERSON, D.B. Proc. Roy. Soc. 267, (1962) p.443.

(80) DOBSON, G. and HUGHES, G. Trans. F. Soc. 57, (1961) p.1117.

(81) ANDERSON, A.R. and HART, E.J. J. Phys. Chem. 65, (1961) p.804.

(82) ANDERSON, .R. and HART, E.J. J. Phys. Chem. 66, (1962) p.70.

(83) CZAPSKI, G. and ALLEN, A.O. J. Phys. Chem. 66, (1962) p.262.

(84) CZAPSKI, G. and SCHWARZ, H.A. J. Phys. Chem. 66, (1962) p.471.

(85) COLLINSON, E. et al. (a) Proc. Chem. Soc., (1962) p.140
(b) Second Int. Congress of Radn. Res., Harrogate, Aug. 5-11 (1962). Abstracts of papers. p.66.

(86) JORBNER, J. and RABANI, J. J.A.C.S. 83, (1961) p.4868.

(87) RABANI, J. J.A.C.S. 84, (1962) p.868.

(88) HAYON, E. Nature 196, (1962) p.533.

(89) DAINTON, F.S. and WATT, W. Nature 195, (1962) p.1294.

(90) PLATZMAN, R.L. Radn. Res. 2, (1955) p.1.

(91) HOARE, D.E. and WALSH, A.D. Trans. F. Soc. 53, (1957) p.1102.

(92) BALDWIN, R.R. and BROOKS, C.T. Trans. F. Soc. 58, (1962) p.1782.

(93) CZAPSKI, G. and JORTNER, J. Nature 188, (1960) p.50.

(94) BRADBURY, N.E. J. Chem. Phys. 2, (1934) p.827.

(95) CURRAN, R.D. and FOX, R.E. J. Chem. Phys. 34, (1961) p.1590.

(96) SCHULZ, G.J. J. Chem. Phys. 34, (1961) p.1778.

(97) PRITCHARD, H.O. Chem. Revs. 52, (1953) p.529.

(98) FERRADINI, C. and KOULKES-PUJO, A.M. Second Int. Congress of Radn. Res., Harrogate, Aug. 5-11, (1962). Abstracts of papers, p.72, and private communidation.

(99) BURTON, M. and KURIEN, K.C. J. Phys. Chem. 63, (1959) p.899.

(100) BENSON, S.W. The foundations of chemical kinetics. McGraw Hill. (1960) p.498.

(101) SWORKSI, T.J. Radn. Res. 2, (1955) p.26.

(102) HOLTHUSEN, H. See GRAY, ref. 21 and 22 refers to Arch. Ges. Physiol. 187, (1921) p.1.

(103) GRAY, L.H. Radn. Res. 1, (1954) p.189.

(104) ALPER, T. and HOWARD-FLANDERS, P. Nature 178, (1956) p.978.

(105) HUTCHINSON, F. Radn. Res. 7, (1957) p.473.

(106) HOWARD-FLANDERS and MOORE, D. Radn. Res. 9, (1958) p.422.